THE SYNTHESIS OF HYDROCARBONS

(REPORT OF THE IMPERIAL FUEL RESEARCH INSTITUTE OF JAPAN, JULY 25, 1935)

BY SHIGERU TSUTSUMI
(REVISED AND EDITED BY ROBERT C. GRASS)

WITH PREFACE BY ROBERT C. GRASS

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Shigeru Tsutsumi[1/]

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PREFACE

In the summer of 1945, when it was evident that invasion of the Japanese home islands was imminent, the U. S. Naval Technical Mission to Japan was established to evaluate the accomplishments of the Japanese in naval technology and related fields. Of primary importance to the object of the mission was the acquisition of the maximum amount of information in the shortest possible time after the country was entered. Each day's delay allowed additional Japanese equipment and documents to be destroyed and made it easier for key Japanese personnel to disappear. With this in mind, the first entry into Japan by mission personnel was made early in September, and the activities of the mission were highly concentrated over the next few months, terminating finally in December.

One of the many phases of the Japanese technical war effort in which mission investigators were interested was the program directed toward obtaining liquid fuels from coal and other sources. The Japanese navy attached tremendous importance to research in this direction, and in 1945 approximately 3,200 persons, including about 400 technically trained personnel, were employed at the First Naval Fuel Depot at Ofuna, where every known phase of fuel and lubricant technology was being investigated. Research and development work involving both direct and indirect coal-hydrogenation processes was also being carried out in such places as the Institute of Fuel Technology at the Imperial University of Kyoto, the Imperial Fuel Research Institute of the Department of Commerce and Industry, the Hokkaido Synthetic Petroleum Co., Inc., and the Tokyo Institute of Physical Chemical Research. The relation of the Imperial Fuel Research Institute to the Japanese economy corresponds rather closely to that of the Bureau of Mines in the United States. In coal hydrogenation investigations conducted there, emphasis was placed on assays and fundamental studies rather than production. It was said that over a hundred Japanese coals had been so studied.

As Japan is extremely deficient in petroleum, it is not surprising to discover that organized effort had been expended to obtain liquid fuels from sources that would otherwise appear fantastic. In attempts to supplement their supplies of motor fuel, so necessary to the prosecution of mechanized warfare, the Japanese investigated the potentialities of such source materials as orange peels, rubber, and pine needles and studied the hydrogenation of coal more extensively than any other nation except Germany. Their rewards for these efforts, however, were meager. Although plants for producing synthetic liquid fuels were constructed and operated, their output fell disastrously short of the magnitude necessary to support the Japanese military machine. Maximum production was attained in 1944, for which the total synthetic fuel output was reported as 1,055,000 barrels, divided among the various processes as follows: hydrogenation (of tars and other oils) = 5,780 barrels; Fischer-Tropsch process = 149,250 barrels; and low-temperature carbonization = 899,970 barrels.

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To provide an insight into Japanese research methods and to determine the direction taken by synthetic fuel research in Japan both before and during World War II, mission investigators obtained a number of papers and reports from the organizations listed above. These papers, of which the following is exemplary, have been translated and carefully examined. For many reasons, the English translations must be regarded with reservations. The conversion of Japanese text to its English equivalent is complicated by extreme language difficulties; in many cases, words do not exist in the one language for ideas expressed in the other. The task was complicated further by a lack of familiarity with the field of synthetic liquid fuels on the part of some of the translators. In addition, it must be emphasized that many of the discussions to be found in these papers were based on theories which, at that time were accepted as valid by most of the scientific world, but which have since been discarded in the light of subsequent experimental evidence. Despite the accompanying qualifications, it is felt that these papers are instrumental in establishing an appreciation of Japanese research efforts in the field of synthetic liquid fuels.

INTRODUCTION

The rapid development of transportation facilities in Japan focused the attention of this country on the possibility of converting the existing coal resources (of which there was an abundance) into liquid fuels, for which there was a constantly increasing demand. Previous work had indicated that this could be accomplished by utilizing one of two processes - the Bergius process, in which high temperatures and high pressures were employed to effect direct liquefaction of the coal, and the Fischer-Tropsch process, in which an indirect liquefaction of coal was accomplished by the production of liquid hydrocarbons from hydrogen-carbon monoxide mixtures. This report describes some investigations into the latter process, which was first developed by Fischer and his colleagues in the Coal Laboratory in Muhlheim, Germany, in 1923. By 1932, these investigators had achieved a 60-percent theoretical yield (152 ml. of liquid hydrocarbons per cubic meter of $2H_2$:1CO synthesis gas) by using a precipitated Co-ThO_2 catalyst.3/ At the same time (1932), Dr. Kita of Kyoto Imperial University and Messrs. Fujimura and Tsuneoka obtained 145 ml. of gasoline (C_5+) per cubic meter of synthetic gas by using a Co-Cu-Th-U catalyst.4/ This report is a description of the experimental results subsequently obtained at the Fuel Research Institute, Kawaguchi City, Saitama, up to 1935.

EXPERIMENTAL

Apparatus

The apparatus used in laboratory-scale studies of the Fischer-Tropsch synthesis is shown schematically in figure 1. Synthesis gas was stored in

3/ Fischer, F., and Koch, H., [Recent Developments of Cobalt Catalysts for the Synthesis of Hydrocarbons]: Brennstoff Chem., vol. 13, No. 4, February 15, 1932, pp. 61-68.

4/ Fujimura, Kenji, and Tsuneoka, Shunzo, [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XII]: Jour. Soc. Chem. Ind. Japan, vol. 35, 1932, p. 1022; supplemental binding pp. 415-416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 198-201.

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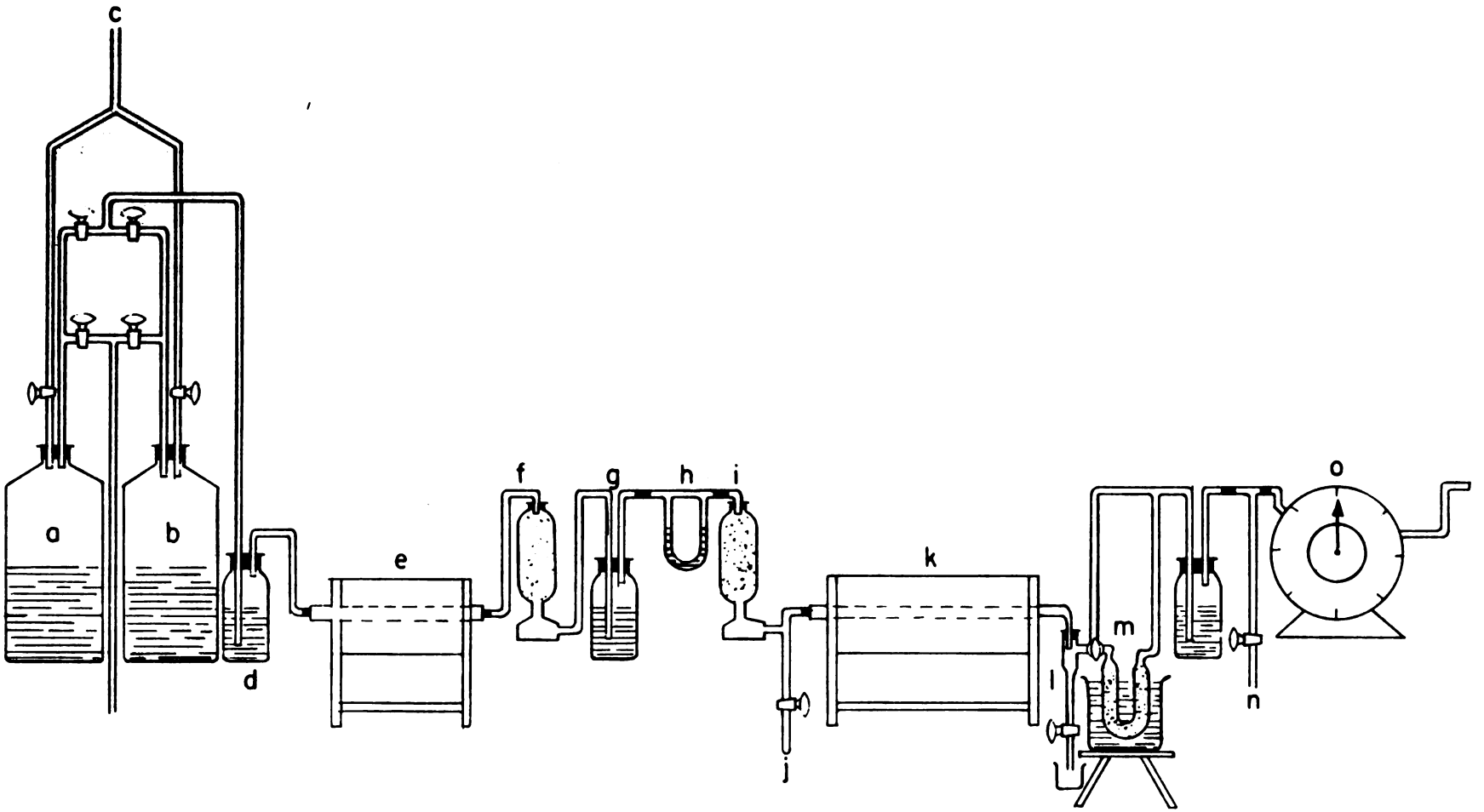

Figure 1.–Laboratory-scale apparatus (6 $m.^3$/hr. throughput) used in studies of the hydrocarbon synthesis.

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the 10-liter bottles, A and B; by proper manipulation of the stopcocks, one bottle could be filled with gas while gas from the other bottle was being used. Synthesis gas leaving the storage bottles was maintained at a constant velocity and was passed through a purification train, where oxygen was eliminated by passage through a solution of pyrogallol (D) followed by a bed of red-hot copper (E); water vapor and carbon dioxide were removed by passage through calcium chloride (F) and potassium hydroxide solution (G). After passing through a manometer (H), the gas was redried over calcium chloride (I) and entered the reaction tube (K), a crystalline quartz tube 2 cm. I.D. and 60 cm. long, heated externally by an electric furnace. The temperature of the furnace midway between the ends was obtained either with platinum:platinum-rhodium thermocouples or with thermometers corrected at the tin and naphthalene points. The oil and water produced were condensed in the burette L, and the uncondensed products were adsorbed in two U-tubes (M; only one shown) containing activated charcoal. The volume of the gas produced was measured by a gasmeter, and the contraction was computed from this value and the volume of gas at the same conditions passed to the reactor from storage bottles A and B. Correction of these calculations for the oxygen and other impurities removed by the purification train was unnecessary, because the synthesis gas was produced from carefully purified materials and generally contained less than 0.2 percent of these contaminants.

Samples of synthesis gas and the product gases were withdrawn at outlets J and N, respectively, for analysis. In addition, to obtain an insight into the quantitative relationships of the synthesis, the product gases were analyzed by means of a Mariott gas-extracting bottle placed after the gas gage. In analyzing the product gas samples, a Hempel gas-analysis apparatus was used; carbon dioxide was absorbed by potassium hydroxide solution, unsaturated hydrocarbons by fuming sulfuric acid, and carbon monoxide by an ammonia solution of cuprous chloride. The hydrogen content was computed by measuring the decrease in volume following combustion over palladized asbestos; the quantity of saturated gaseous hydrocarbons was measured by determining the amounts of hydrogen and carbon dioxide produced by combustion.

As will be shown later, the synthesis of hydrocarbons from carbon monoxide and hydrogen is very sensitive to temperature; hence, particularly close attention was directed to the temperature distribution within the converter. The heating element used in this equipment consisted of a Nichrome coil 50 cm. long. In order to study the temperature distribution in the converter, heating was continued until the center of the converter was maintained at a constant temperature of 200° C. Temperature readings were then taken at intervals of 2 cm. from the center. The constant temperature section was found to lie within 4 cm. on each side of the center; at a point 12 cm. from the center the temperature was lower by 3° C. A large amount of catalyst could not be placed in this 8-cm. zone of constant converter temperature, however, because a thick layer of catalyst makes a uniform catalyst temperature very difficult to obtain; because the hydrocarbon synthesis is violently exothermic, a thick layer of catalyst favors the formation of local hot spots in the catalyst bed. Hence, in the experiments to be described, the catalyst was spread over a distance of 12 cm. on each side of the center of the converter. The temperature at the center of the converter was assumed to be the average reaction temperature with a possible deviation of $\pm$ 3° C.

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Method of Yield Determination

The oil and water phases condensed in burette L were mutually saturated and contained dissolved oxygen-containing compounds such as alcohols, acetone, and fatty acids produced by secondary reactions. The volumes of the oil and water phases were measured directly in the burette, which was graduated in units of 0.1 ml. Approximately 100 liters of synthesis gas were used in each experiment; thus, an error of 0.02 ml. in reading the burette amounted to only about 0.2 ml. when calculated on the basis of a cubic meter of synthesis gas.

Volatile products, which were adsorbed in the two glass U-tubes containing activated charcoal, were recovered by revaporizing with superheated steam at 200° to 250° C. The recovery apparatus is shown in figure 2. In this procedure, stopcock C was first closed, and the U-tubes were heated to 200° to 250° C. in cottonseed oil. Stopcock C was then opened, and superheated steam was injected. (Air-free steam is necessary in order to prevent loss of product.) The distillate vapors were passed through the water-cooled condenser, E, and collected in receiver F. The receiver was a 10 to 20 ml. burette, graduated to read in 0.1 ml., with a stopcock bottom. The oil floated in the upper part of the burette, and the excess water was siphoned out of a side tube attached to the lower part of the burette.

Synthesis Gas

The carbon monoxide in the synthesis gas was produced by dripping formic acid into sulfuric acid that had been heated to 150° to 180° C. The product was washed with potassium hydroxide solution to remove carbon dioxide. Commercial pressurized hydrogen was used after purification by potassium permanganate and potassium hydroxide solution.

Catalysts

Nickel and cobalt catalysts were first prepared from imported Merck or Kahlbaum reagents, but subsequent catalysts prepared from indigenous reagents produced by Kato, Konishi, and Takeda showed almost no difference in activity. The pure native products, such as those listed below, were chiefly used in these experiments.

Nickel nitrate	Kahlbaum product, Kato product (guaranteed)
Cobalt nitrate	Kahlbaum product, Kato product (guaranteed)
Thorium nitrate	Konishi (pure) product
Uranium nitrate	Kato product (guaranteed)
Manganese nitrate	Kahlbaum product
Silver nitrate	Konishi (pure) product
Copper nitrate	Kato product (guaranteed)

Salts such as manganese nitrate and copper nitrate, which are extremely hygroscopic, were dissolved and used as standard solutions. To improve its thermal conductivity, the catalyst was smeared on small fragments of copper or iron gauze before charging into the reaction tube. As carriers, two or three types of diatomaceous earth found in different localities were employed after dissolving out their iron impurities with strong nitric acid, washing with hot water until neutral, and drying at about 120° C.

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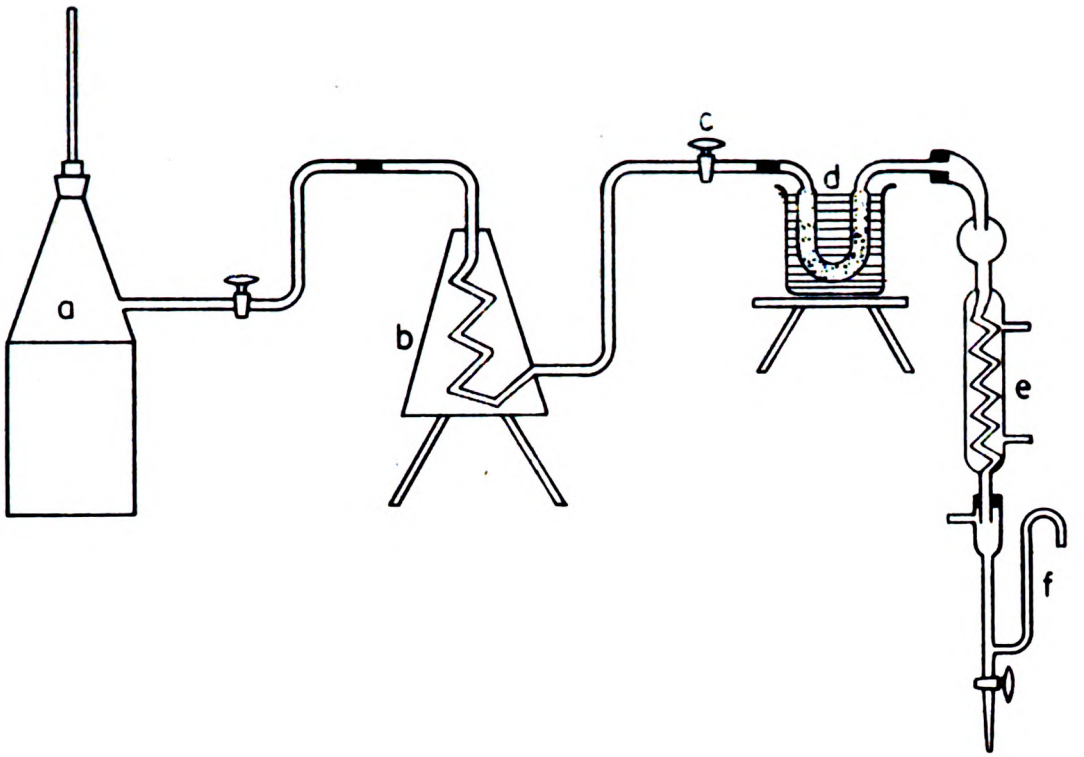

Figure 2.- Steam stripping of light-oil fraction from activated charcoal adsorption tube.

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HYDROCARBON YIELD AS A FUNCTION OF OPERATING VARIABLES

The yield of gasoline (C_5+ hydrocarbons) is affected by the following operating variables: (1) reaction temperature, (2) gas velocity, and (3) composition of the synthesis gas. Results of experiments to determine the effects of these variables are described below.

Effects of the Reaction Temperature

The formation of a paraffin series of hydrocarbons from CO and H_2 may be represented by the following equations:

$$CO + 3H_2 = CH_4 + H_2O + 59.8 \text{ kcal.}$$

$$2CO + 5H_2 = C_2H_6 + 2H_2O + 105.5 \text{ kcal.}$$

$$3CO + 7H_2 = C_3H_8 + 3H_2O + 152.5 \text{ kcal.}$$

$$5CO + 11H_2 = C_5H_{12} + 5H_2O + 249.5 \text{ kcal.}$$

$$8CO + 17H_2 = C_8H_{18} + 8H_2O + 384 \text{ kcal.}$$

The energies liberated in these reactions were calculated, on the basis of Francis'[5] thermodynamic values, to be as follows:

	ΔF	t, °C. ($\Delta F=0$)
CH_4	-52,830 + 60.3 T	603
C_2H_6	-94,660 + 121.5 T	506
C_3H_8	-135,340 + 181.15 T	474
C_4H_{10}	-176,020 + 240.8 T	458
C_5H_{12}	-216,700 + 300.45 T	448
C_8H_{18}	-338,740 + 479.4 T	434

In general, chemical reactions act in the direction in which the liberated energy, ΔF, decreases; that is, the more negative the value ΔF, the greater the degree to which the reaction will be completed. By considering the values listed above, it is evident that the lower the value of T (reaction temperature in absolute units), the more the reactions are favored from left to right. The temperature at $\Delta F=0$, that is, the temperature at which the direction of the reaction shifts from right to left, decreases as the higher members of the series are formed. Thus, the lighter, gaseous hydrocarbons are stable at fairly high temperatures, but the heavier, liquid hydrocarbons are stable only at low temperatures. Accordingly, the formation of liquid hydrocarbons (C_5+)

5/ Francis, A. W., The Free Energies of Some Hydrocarbons: Ind. Eng. Chem., vol. 20, No. 3, March 1928, pp. 277-282.

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is limited to temperatures below 448° C. However, the rate of reaction increases with increasing temperature, and although the effect of temperature on the production of liquid hydrocarbons is disadvantageous, especially in the case of a reaction that proceeds to only a small degree, it is sometimes necessary to increase the temperature to obtain a practical reaction rate. Designating the rate of reaction of carbon monoxide as R and the percentage transformed into liquid hydrocarbons as L, it is evident that the yield of gasoline will be governed by the product of RxL with a given synthesis gas. In view of the fact that increasing the reaction temperature tends to both increase and decrease the yield of liquid hydrocarbons by two different effects, a value of T should be expected at which the value RxL is a maximum. Fischer,[6] in his report, succeeded in lowering the reaction temperature to 220° C. with a cobalt catalyst but considered 270° C. as the most suitable. Erdley and Nash[7] established the most practicable temperature for Co-Cu-Al_2O_3 catalyst as 280° to 290° C. and did not acknowledge reactions below 230° C. Smith[8] placed 275° C. as the most appropriate for Co-Cu-Mn catalysts, and Kodama[9] designated 250° C. as that best suiting Co-Cu-Th catalysts. Whereas Smith[10] and Berl and Jungling[11] claimed that the higher hydrocarbons were produced at higher reaction temperatures, Fischer and Koch[12] established in their study of nickel and cobalt catalysts that the most suitable temperature for the production of liquid hydrocarbons was about 200° C. and that, as the temperature increased, the formation of gaseous hydrocarbons and carbon dioxide was increased and that of liquid hydrocarbons decreased. Watanabe, Morikawa, and Igawa[13] used weight calculations to theorize on the effects of reaction temperature upon the liquid hydrocarbon yield.

6/ Fischer, F. and Tropsch, H., [The Synthesis of Hydrocarbons at Ordinary Pressures from the Gasification Products of Coal]: Brennstoff Chem., vol. 7, No. 7, April 1, 1926, pp. 97-104.

7/ Erdley, A., and Nash, A. W., A Contribution to Our Knowledge of the Catalysts Used in the Synthesis of Higher Hydrocarbons from Water Gas: Jour. Soc. Chem. Ind. (Transactions), vol. 47, Aug. 10, 1928, pp. 219-223.

8/ Smith, D. F., Davis, J. D., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas, I: Ind. Eng. Chem., vol. 20, No. 5, May 1928, pp. 462-464.

9/ Kodama, Shinjiro, [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure, III. Preparation of Liquid Hydrocarbons with a Cobalt-Copper-Thoria Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 959; supplemental binding (in German), pp. 285-286.

10/ Smith, D. F., Hawk, C. O., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas II: Ind. Eng. Chem., vol. 20, No. 12, December 1928, pp. 1341-1348.

11/ Berl, E., and Jungling, K., [Synthesis of Higher Hydrocarbons from Water Gas at Atmospheric Pressure]: Ztschr. angew. Chem., vol. 43, 1930, pp. 435-440.

12/ Fischer, F., and Meyer, K., [The Applicability of Nickel Catalysts to the Hydrocarbon Synthesis]: Brennstoff Chem., vol. 12, No. 12, June 15, 1931, pp. 225-232.

13/ Watanabe, S., Morikawa, K., and Igawa, S., [The Synthesis of Hydrocarbons by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure II. The Effect of Temperature on the Synthesis]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 891; supplemental binding, pp. 385-389.

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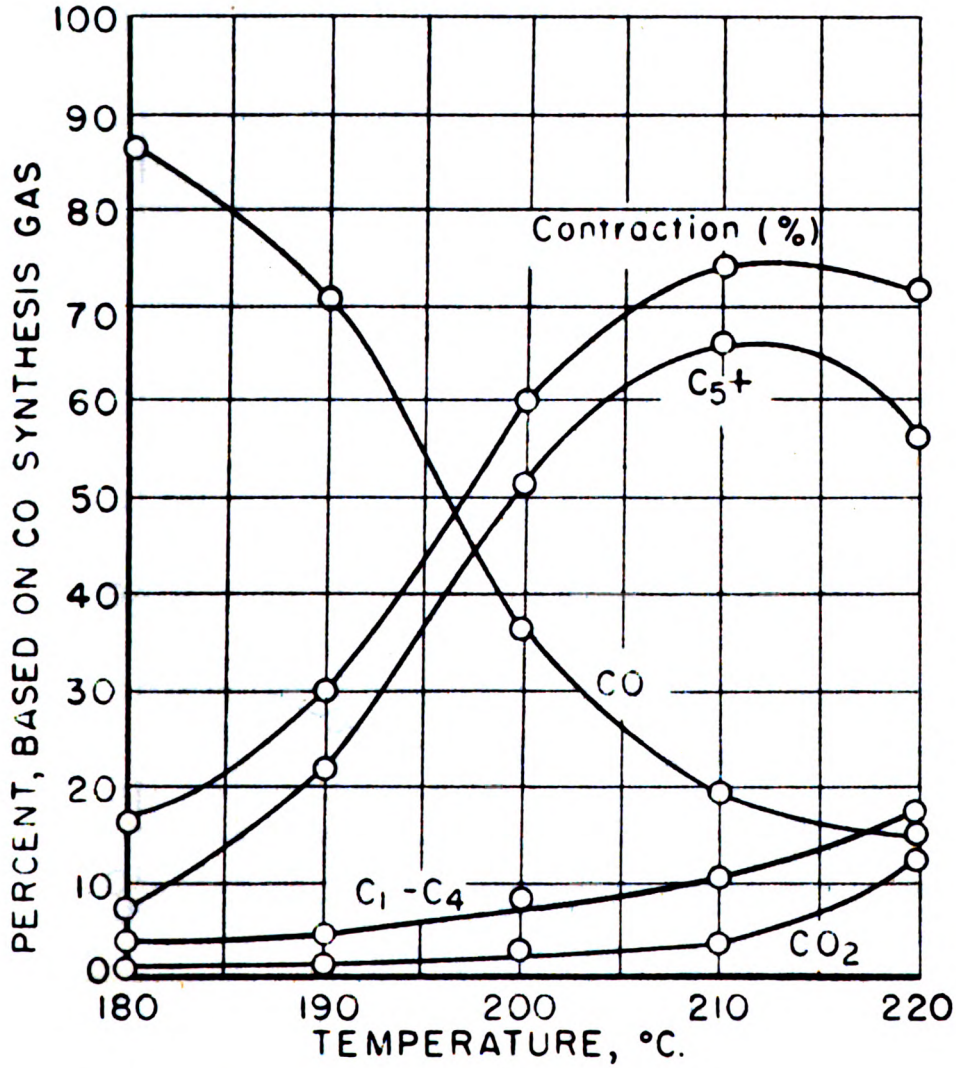

Figure 3.– Effect of reaction temperature on hydrocarbon synthesis.

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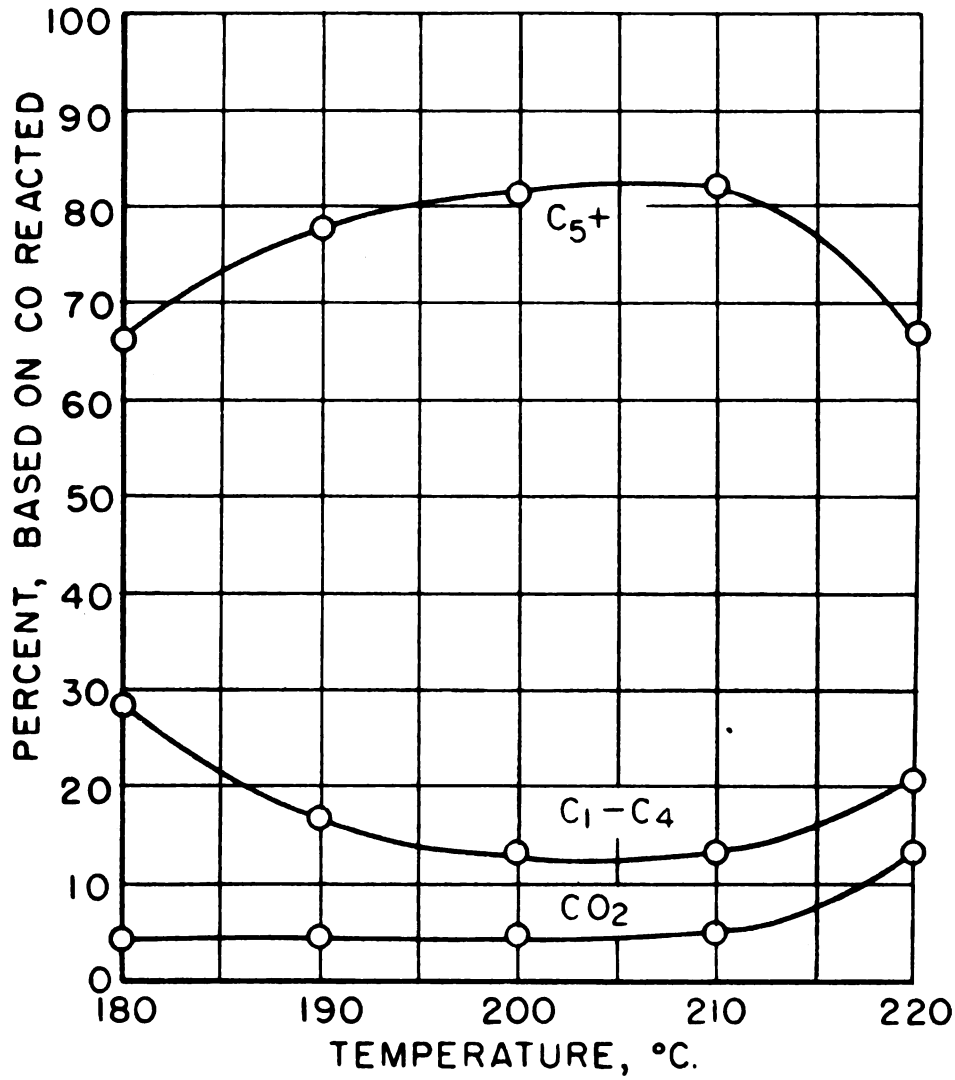

Figure 4.- Effect of reaction temperature on hydrocarbon synthesis

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Experimental Methods and Results

The catalyst used was 100 Co:10 Cu:12 U_3O_8:100 diatomaceous earth, corresponding to 3 gm. Co; 72.0 liters of synthesis gas was used at a gas velocity of 6.0 l./hr. at each of the five reaction temperatures employed, namely, 180°, 190°, 200°, 210°, and 220° C. Table 1 shows the yield of liquid products and the results of the analyses of the product gases for a 36-liter product-gas sample.

From the analyses of the synthesis gas and product gas and from the gas contraction, the percentage distribution of carbon among the carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons in the product gas was calculated based on the carbon monoxide in the synthesis gas. The difference between the sum of these three values and 100 was taken as the percentage of carbon monoxide that had been converted to gasoline. The formation of unsaturated hydrocarbons (C_mH_n) was so small as to fall within the experimental error of the determination and, therefore, was not considered in the calculations. The results of these calculations are listed in table 2 and plotted graphically in figures 3 and 4.

A summary of the above experimental results shows that:

(A) The ratio of carbon monoxide conversion to hydrogen conversion increased with increase in temperature.

(B) On the basis of carbon monoxide in the synthesis gas, the percentage of carbon monoxide converted to carbon dioxide and the percentage converted to gaseous saturated hydrocarbons increased with increasing temperature; the percentage of carbon monoxide converted to gasoline began to increase at 180° C. and passed through a maximum between 210° and 220° C.

(C) On the basis of carbon monoxide reacted, the percentage of carbon monoxide converted to carbon dioxide increased gradually with temperature to 210° C., where it increased rapidly; the percentage converted to gaseous saturated hydrocarbons decreased with increase in temperature and showed a minimum value at about 210° C.; conversely, the percentage converted to gasoline increased progressively from 180° C. and reached a maximum at 210° C., decreasing rapidly to 220° C.

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TABLE 1. - Effect of reaction temperature

(72.0 l. of synthesis gas at a velocity of 6 l./hr. used at each temperature)

Experiment number	Reaction temperature, ° C.	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./m.^{3} of synthesis gas		Product gas composition, percent						
		CO	H_2	N_2		Gasoline (C_5+)	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
1.....	180	30.4	64.5	5.1	16.2	20.8	55.6	0.2	0.2	31.4	61.4	0.4	3.53	6.4
2.....	190	30.6	64.4	5.0	30.0	52.5	95.2	.6	-	31.0	60.4	.7	3.00	6.9
3.....	200	32.6	64.0	3.4	60.4	110.6	150.5	2.6	-	30.0	56.1	2.4	2.97	8.9
4.....	210	32.5	65.2	2.3	74.0	138.0	180.5	4.6	.2	24.4	54.2	7.7	1.72	8.9
5.....	220	32.6	65.0	2.4	71.8	125.5	195.6	12.8	.2	17.6	45.0	16.2	1.24	8.2

TABLE 2. - Effect of reaction temperature

(72.0 l. of synthesis gas at a velocity of 6 l./hr. used at each experiment)

Experiment number	CO conversion, percent	H_2 conversion, percent	Carbon distribution						
			Percent of CO in synthesis gas				Percent of CO reacted		
			CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_5+)	CO_2	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_5+)
1.....	13.5	20.2	0.6	86.5	3.9	7.4	4.5	28.9	66.6
2.....	29.1	34.3	1.4	70.9	4.8	22.0	4.8	16.5	78.7
3.....	63.6	65.3	3.2	36.4	8.7	51.7	5.0	13.7	81.3
4.....	80.5	78.4	3.7	19.5	10.6	66.2	4.6	13.2	82.2
5.....	84.8	80.5	11.1	15.2	17.4	56.3	13.1	20.5	66.4

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Discussion

Although the rate of reaction between carbon monoxide and hydrogen was a maximum at 220° C., the maximum yield of gasoline was obtained at 210° C., the result of an acceleration in the production of carbon dioxide and gaseous saturated hydrocarbons beyond 210° C. This is evident from inspection of figure 4, which shows that the production of gaseous hydrocarbons decreased from 180° to 205° C., at which point it increased. However, the value "n" has been defined as the number of carbon atoms in the average gaseous hydrocarbon product, and table 1 shows that this value decreased continuously with increasing temperature, suggesting that the production of gaseous hydrocarbons should increase continuously with increasing temperature instead of first decreasing in the manner shown in figure 4. The cause of this initial decrease may lie in the following theory.

The carbidic carbon produced by reaction of carbon monoxide with the catalyst is hydrogenated to such free radicals as $\dot{C}H$-, $\dot{C}H_2$, and $\dot{C}H_3$, which, at about 180° C., polymerize very slowly. The formation of liquid hydrocarbons, therefore, is small and is accompanied by a relatively large formation of low-molecular-weight gaseous hydrocarbons. As the temperature is increased from 180° to 210° C., the rate of polymerization of the free radicals increases so that more liquid hydrocarbons are produced at the expense of the low-molecular-weight products. However, the distribution of free radicals produced by the hydrogenation of carbide also depends on the reaction temperature. Thus, at about 180° C., large amounts of $\dot{C}H$- and $\dot{C}H_2$ are produced with small amounts of $\dot{C}H_3$. Because the polymerization rate is slow, these free radicals are combined mainly in the form of gaseous hydrocarbons of C_2+. Very little methane is formed. At higher temperatures, $\dot{C}H_3$ is produced along with $\dot{C}H$- and $\dot{C}H_2$; the structure of the $\dot{C}H_3$ radical makes the chances of polymerization very much smaller than in the case of $\dot{C}H_2$ and $\dot{C}H$- radicals, and thus, at the higher temperatures, considerable methane is produced. As the polymerization rate is greater at the higher temperatures, more liquid hydrocarbons are formed from $\dot{C}H$- and $\dot{C}H_2$ radicals. Accordingly, the average molecular weight of the gaseous products is less at higher temperatures than at lower temperatures. Thus, from 180° to 210° C., one has the apparently incompatible cases of the value of "n" decreasing as the production of liquid hydrocarbons increases and the production of gaseous hydrocarbons decreases.

It has been shown previously that from thermodynamic considerations the production of liquid hydrocarbons is favored by decreasing temperatures. The apparent anomaly regarding the increase in gasoline production observed with increasing temperature in figure 4 may be resolved by recalling that thermodynamic considerations are based upon the assumption that each reaction attains its theoretical equilibrium, whereas, under actual experimental conditions, reaction equilibrium was not reached at low temperatures. At temperatures below 210° C., the speed at which the reaction approaches its theoretical equilibrium is quite slow.

It is recognized, of course, that on the basis of this experimental evidence alone it is not possible to determine the maximum possible molecular weight of the liquid hydrocarbon product nor the exact optimum temperature at which it may be obtained. It may be said, however, that the optimum temperature is certainly not of the order of 180° C. where the speed of reaction is low.

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From these considerations it may be possible to reconcile the apparent differences between the opinions of Smith[14] and Berl and Jüngling,[15] who said that high-molecular-weight hydrocarbons were favored by high temperatures, and that of Fischer,[16] who said that high-molecular-weight hydrocarbons were favored by low temperatures, if these investigators were referring to different temperature ranges. Thus, if Fischer's "low" temperature was 210° to 220° C. and corresponded to the "high" temperature of Smith and Berl and Jüngling, the results of these investigators are compatible. Fischer considered a reaction temperature of about 200° C. as being the optimum, as compared to the optimum temperature of 250° C. selected by Smith and Berl and Jüngling. In view of the previous discussion, this difference may originate in two different basic considerations. Thus, when the reaction takes place at "high" temperatures of about 250° C., the rate of reaction is high and the quantity of gaseous hydrocarbons produced is great, but, with time, because of the deposition of free carbon on the catalyst, the activity of the catalyst is gradually diminished, with a corresponding decrease in hydrogenation of carbide to form free radicals. As, however, the rate of the polymerization of the free radicals that are present is great at this high temperature, solid paraffins or liquid hydrocarbons of high boiling points are produced in accordance with the view point of Smith and Berl and Jüngling.

As indicated by table 1, the optimum temperature for production of gasoline (C_5+) is 210° ± 5° C. The extreme temperature-sensitivity of the reaction is a result of the poor thermal conductivity of the catalyst. The utilization in the catalyst of a carrier of diatomaceous earth, a poor conductor of heat, makes transmission of the heat of reaction (an extremely great value) outside the catalytic system very difficult. In addition, because of local superheating at the point of activation, the slightest amount of heat from external sources causes a phenomenal increase in the temperature of the catalyst. (This shows that the activity of the catalyst is extremely high, requiring only a small activation energy.)

Effects of the Gas Velocity

At a given temperature, and using a given quantity of catalyst, the extent of reaction of carbon monoxide and hydrogen tends to increase with decrease in velocity of the gas (increase in contact time). The rate of polymerization of the CH-, CH_2, and CH_3 radicals produced from the carbon monoxide and hydrogen is increased, however, to a smaller degree than that at which hydrogen is added to form methane; therefore, as the velocity of the gas is decreased, the methane-producing reaction is accelerated, and, when this value is large compared to the increase in the extent of reaction between carbon monoxide and hydrogen, the yield of liquid hydrocarbons is reduced. Hence, an optimum gas velocity is to be expected in the production of liquid hydrocarbons. Fischer and Tropsch,[17] by suitably increasing the gas velocity, found that it was possible to prevent the methane-producing reaction almost entirely and stated that an optimum gas velocity in the production of liquid

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14/ Work cited in footnote 11, p. 6.
15/ Work cited in footnote 12, p. 6.
16/ Work cited in footnote 13, p. 6.
17/ Work cited in footnote 6.

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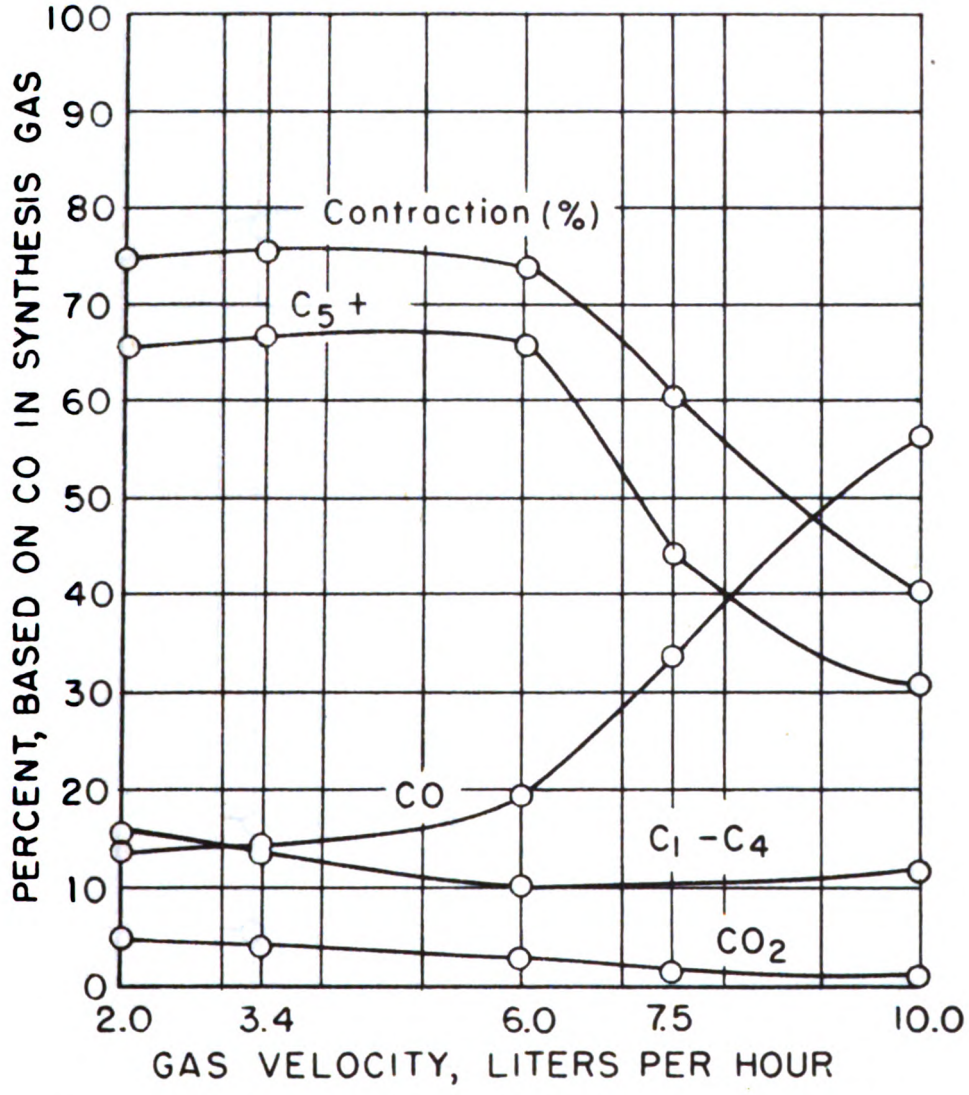

Figure 5. – Effect of synthesis gas velocity on hydrocarbon synthesis.

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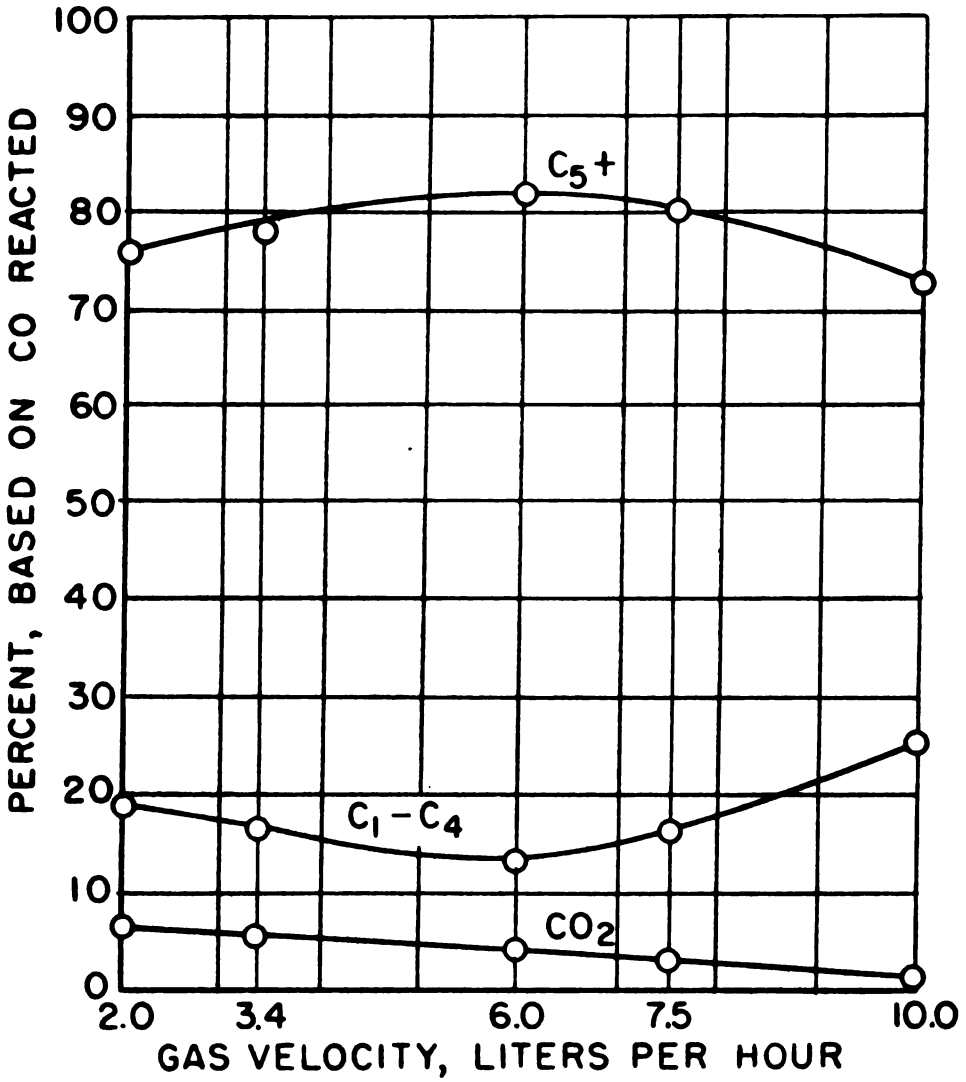

Figure 6. – Effect of synthesis gas velocity on hydrocarbon synthesis.

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hydrocarbons should exist. Kodama[18] obtained similar results, whereas Smith[19] declared that, with decrease in the velocity of the gas, the yield of liquid hydrocarbons increased.

Experimental Methods and Results

Five velocities of feed gas, namely, 2.0, 3.4, 6.0, 7.5, and 10.0 l./hr., were used in experiments with 100 Co:10 Cu:12 U_3O_8:100 diatomaceous earth catalyst, corresponding to 3 gm. of cobalt and a reaction temperature of 210° C. In each case, 72.0 liters of synthesis gas was used, except in the experiment involving a velocity of 2.0 l./hr., in which 36.0 l. of gas was used. The yields of gasoline (C_5+) and water and the gas contraction were measured, and the product gases from half the initial quantity of feed gas were analyzed; the results are shown in table 3.

From analyses of the synthesis and product gases and from the gas contraction, the percentage distribution of carbon among the carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons contained in the product gas (based upon the carbon monoxide in the synthesis gas) was obtained. Subtracting the sum of these three values from 100 yielded the percentage of carbon monoxide converted to gasoline. These results are shown in table 4.

The data given in table 4 are plotted in figures 5 and 6. These results show that:

(A) The rate of reaction between carbon monoxide and hydrogen increased with decrease in gas velocity, the largest value being at the smallest flow rate used, 2.0 l./hr.; the degree of conversion of carbon monoxide in the synthesis gas to carbon dioxide and gaseous saturated hydrocarbons increased with decrease in velocity.

(B) The degree of conversion of carbon monoxide to carbon dioxide based on carbon monoxide reacted increased with decrease in velocity. The degree of conversion to gaseous saturated hydrocarbons decreased as the gas velocity increased above 2.0 l./hr., showed a minimum value at 6.0 l./hr., and increased again as the velocity was raised to 7.5 and 10.0 l./hr.

(C) The yield of gasoline per cubic meter of synthesis gas was approximately the same at velocities from 3.4 to 6.0 l./hr. and decreased gradually with either increase or decrease in velocity.

18/ Kodama, Shinjiro: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 362. (Reference could not be located.)

19/ Work cited in footnote 8.

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TABLE 3. - Effect of gas velocity

(Reaction temperature = 210° C.; 72.0 l. of synthesis gas used in each case, except as noted)

Experiment number	Gas velocity, l./hr.	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./m.^{3} of synthesis gas		Product gas composition, percent						
		CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
6a/.....	2.0	32.5	64.0	3.5	74.8	135.6	190.6	6.5	0.2	18.2	48.2	13.6	1.48	13.3
7.....	3.4	32.2	65.0	2.8	75.5	139.2	195.2	5.6	.1	19.6	52.0	11.7	1.58	11.0
8.....	6.0	32.5	65.2	2.3	74.0	138.0	180.5	4.6	.2	24.4	54.2	7.7	1.85	8.9
9.....	7.5	32.6	65.2	2.2	60.5	102.2	148.6	1.6	.2	27.4	60.0	4.7	1.91	6.1
10.....	10.0	32.5	64.8	2.7	40.6	64.4	118.2	0.4	.2	30.8	61.7	2.8	2.34	4.1

a/ 36.0 liters of synthesis gas used.

TABLE 4. - Effect of gas velocity

(Reaction temperature = 210° C.; 72.0 l. of synthesis gas used in each case, except as noted)

Experiment number	Gas velocity, l./hr.	CO conversion, percent	H_2 conversion, percent	Carbon distribution						
				Percent of CO in synthesis gas				Percent of CO reacted		
				CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})	CO_2	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})
6a/.....	2.0	85.9	81.4	5.0	14.1	15.6	65.3	5.8	18.2	76.0
7.....	3.4	85.1	80.4	4.3	14.9	14.1	66.7	5.1	16.6	78.3
8.....	6.0	80.5	78.4	3.7	19.5	10.6	66.2	4.6	13.2	82.2
9.....	7.5	66.8	63.6	1.9	33.2	10.9	44.0	2.8	16.3	80.9
10.....	10.0	43.7	43.4	.7	56.3	12.0	31.0	1.6	25.2	73.2

a/ 36.0 liters of synthesis gas used.

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Discussion

In (C) above, the yield of gasoline based on the carbon monoxide in the synthesis gas was observed to increase as the gas velocity was decreased from 10 l./hr.; from 6.0 to 3.4 l./hr., however, the yield was approximately constant, and, as the gas velocity was decreased still further, the gasoline yield decreased. This effect is a result of an increase in production of carbon dioxide and gaseous hydrocarbons, which at 3.4 l./hr. reaches about the same value as the increase in the total conversion; whereas, at a gas velocity of 2.0 l./hr. the production of carbon dioxide and gaseous hydrocarbons is increased to an even greater degree. Conversely, as the gas velocity is increased beyond 6 l./hr., although the production of carbon dioxide and gaseous hydrocarbons is reduced, the extent of reaction between carbon monoxide and hydrogen is reduced to an even greater extent, and the yield of gasoline decreases with increase in gas velocity.

As the gas velocity is increased beyond 2 l./hr., the degree of conversion of carbon monoxide to gaseous saturated hydrocarbons decreases and passes through a minimum value at 6.0 l./hr. Simultaneously, the value (n) of the average number of carbon atoms in the gaseous saturated hydrocarbon molecules increases with increase in gas velocity. Comparison of these results with those obtained in studies of the reaction temperature show that when the gas velocity is high, effects are produced similar to those at temperatures below 210°; conversely, when the velocity is low, changes occur in the production of carbon dioxide and gaseous saturated hydrocarbons with changes in the value (n) of the latter similar to those observed at temperatures above 210°.

These results suggest that the time required for the hydrogenation of $\dot{C}H$-, $\dot{C}H_2$, and $\dot{C}H_3$ radicals to such gaseous hydrocarbons as methane and ethane is much larger than the time required for their polymerization. Thus, the variation of (n) with gas velocity may be explained on the following basis: When the gas velocity is low (2.0-3.4 l./hr.), not only is the production of methane by secondary reactions enhanced, but, in addition to the production of $\dot{C}H$- and $\dot{C}H_2$ radicals, a large quantity of $\dot{C}H_3$ is produced. The value (n) is small, therefore, because $\dot{C}H_3$ is hydrogenated to such gaseous hydrocarbons as methane and ethane. At high gas velocities, $\dot{C}H$- and $\dot{C}H_2$ are produced almost exclusively, and, because the contact time is short, most of the $\dot{C}H$- and $\dot{C}H_2$ radicals are transformed into gaseous hydrocarbons instead of polymerizing further to form liquid hydrocarbons. Hence, (n) becomes greater in value.

To eliminate long contact times and the attendant large production of carbon dioxide and gaseous saturated hydrocarbons, the relative area presented by the catalyst layers must be decreased. This may be accomplished by enlarging the cross section of the reaction tube, thereby increasing the volume of synthesis gas contacting the catalyst and decreasing the contact time. This also serves to maintain the original $CO:H_2$ ratio, deviation from which, by reaction in the first part of the reactor, is deleterious to the desired reaction in the later portion of the reactor.

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Effects of the Synthesis Gas Composition

From the general equation for the production of paraffin hydrocarbons from carbon monoxide and hydrogen,

$$n\,CO + (2n + 1)H_2 = C_nH_{2n+2} + nH_2O$$

the quantities of carbon monoxide and hydrogen combining chemically in the case of each homologue are as follows:

n	Homologue	Boiling point, °C.	$\frac{2n+1}{n}$ (usage ratio, H_2/CO)
1	methane	-164.0	3.00
2	ethane	- 93.0	2.50
3	propane	- 45.0	2.33
4	butane	+ 0.6	2.25
5	pentane	+ 36.0	2.20
6	hexane	+ 69.0	2.17
7	heptane	+ 98.3	2.14

For the production of those paraffins (C_{5+}) normally in a liquid state at ordinary temperatures, the H_2:CO ratio should be maintained below 2.2, as an increase above this value favors the production of gaseous methane, ethane, and propane.

The composition of the synthesis gas may be related to loss of catalyst activity in the following manner: (1) The active centers of the catalyst may be covered by high-boiling hydrocarbons, and (2) carbon may be deposited on the catalyst by the reaction $2CO = C + CO_2$ and by decomposition of synthesis products. The production of high-boiling hydrocarbons (1) is caused by very rapid polymerization of the free radicals, CH-, CH_2, and CH_3, compared to the much slower rate of addition of hydrogen. This tendency may be depressed by using an appropriate excess of hydrogen, the presence of which would also tend to liberate the carbon deposited according to scheme (2). Thus, although too high a concentration of hydrogen is undesirable because it favors the production of gaseous hydrocarbons and reduces the yield of liquid hydrocarbons, it is obvious that from the standpoint of increased catalyst life too low a concentration cannot be tolerated; accordingly, an optimum gas composition must exist. Fischer and Tropsch[20/21/] used $1H_2$:1CO water gas at first. However, consideration of the equation for the production of paraffin hydrocarbons from carbon monoxide and hydrogen shows that this composition is not suitable for the production of compounds in the desired molecular-weight range; furthermore, this H_2:CO ratio decreased the life of the catalyst, and the use of

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20/ Fischer, F., and Tropsch, H., [The Synthesis of Liquid Hydrocarbons]: Brennstoff Chem., vol. 8, No. 1, Jan. 1, 1927, pp. 1-5. (First delivered as a paper before the International Coal Conference, Pittsburgh, Pa., on Nov. 17, 1926.)

21/ Fischer, F., and Tropsch, H., [Development of the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Ordinary Pressures]: Brennstoff Chem., vol. 11, No. 24, Dec. 15, 1930, pp. 489-500.

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$2H_2$:1CO gas was advocated. Elvins[22] considered $1H_2$:1CO gas as most suitable and stated that a surplus of hydrogen enhanced the production of lighter hydrocarbons and water. Erdley and Nash,[23] too, found that surplus hydrogen favored the production of lighter hydrocarbons, and that a surplus of carbon monoxide decreased the catalyst life rapidly; thus, Kodama[24] first used $1H_2$:1CO gas, considering it as the most suitable. Kodama and Fujimura,[25] in an experiment with a Co-Cu-MgO catalyst, used $1.65H_2$:1CO gas and found the yield of liquid hydrocarbons was reduced and the production of water was increased. Fujimura and Tsuneoka[26] found that although surplus carbon monoxide had no ill effect on the synthesis of liquid hydrocarbons, a surplus of hydrogen was extremely harmful in this reaction.

Experimental Methods and Results

By using a 100 Co:5 Cu:12 U_3O_8:100 diatomaceous earth catalyst (corresponding to 3 gm. of cobalt), a gas velocity of 6.0 l./hr., H_2:CO ratios of 3, 2.5, 2.0, 1.5, and 1 (72.0 l. of synthesis gas for each ratio), by measuring the gasoline (C_{5+}) and water yields and the gas contraction in each case, and by analyzing the last 36.0 l. of the product gases in each experiment, the results shown in table 5 were obtained.

From the gas contraction and from the analyses of the synthesis and product gases, the rates of reaction of carbon monoxide and hydrogen were obtained. The percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons were calculated on the basis of the carbon monoxide in the synthesis gas, and the difference between their sum and 100 was taken as the percentage of carbon monoxide converted into gasoline (C_{5+}). The results are tabulated in table 6.

22/ Elvins, O. C., Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen: Jour. Soc. Chem. Ind. (Transactions), vol. 46, Dec. 30, 1927, pp. 473-478.

23/ Work cited in footnote 7.

24/ Work cited in footnote 10, p. 6.

25/ Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure, X. The Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 628; supplemental binding pp. 384-386; Sci. Papers Inst. Phys. Chem. Research, vol. 17, Nos. 333-338, pp. 11-21.

26/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XIX. Composition of the Initial Gas Mixture]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1049; supplemental binding pp. 463-467; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 103-112.

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TABLE 5. - Effect of synthesis gas composition

(Gas velocity = 6.0 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment number	Temperature, °C.	H_2:CO	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./$m.^3$ of synthesis gas		Product gas composition, percent						
			CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
11A.....	180	3:1	24.0	73.2	2.8	61.5	107.1	152.4	0.8	0.2	4.4	77.4	9.6	1.80	7.6
11B.....	190	3:1	24.2	73.2	2.6	67.2	76.2	171.4	1.0	-	2.3	65.1	23.5	1.12	8.1
11C.....	200	3:1	24.0	73.2	2.8	72.0	52.3	191.4	1.8	-	.2	50.5	37.5	1.08	10.0
12.....	200	2.5:1	30.2	67.0	2.8	76.2	139.5	185.0	2.0	.1	18.2	55.7	13.2	1.35	10.8
13.....	200	2:1	32.4	64.8	2.8	78.6	143.7	190.3	3.0	.1	24.0	49.8	10.8	1.58	12.3
14.....	200	1.5:1	40.2	57.5	2.3	75.4	137.5	166.6	3.4	.2	43.2	40.9	3.7	2.57	8.6
15.....	200	1:1	48.8	48.2	3.0	64.4	107.1	166.0	3.6	.2	58.8	25.4	1.5	3.03	10.5

TABLE 6. - Effect of synthesis gas composition

(Gas velocity = 6.0 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment number	H_2:CO	CO conversion, percent	H_2 conversion, percent	Carbon distribution							
				Percent of CO in synthesis gas				Percent of CO reacted			
				CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})	CO_2	C_nH_{2n+2} (C_1-C_4)	CO_2+ C_nH_{2n+2}	Gasoline (C_{5+})
11A.....	3:1	92.9	59.3	1.3	7.1	27.7	63.9	1.4	29.8	31.2	68.8
11B.....	3:1	96.9	70.8	1.4	3.1	35.7	59.8	1.4	36.8	38.2	61.8
11C.....	3:1	99.8	80.3	2.1	.2	47.3	50.4	2.1	47.3	49.4	50.6
12.....	2.5:1	85.7	80.2	1.6	14.3	14.0	70.1	1.9	16.3	18.2	81.8
13.....	2:1	84.1	83.2	2.0	15.9	11.3	70.8	2.4	13.4	15.8	84.2
14.....	1.5:1	73.6	82.5	2.1	26.4	5.1	66.4	2.9	6.9	9.8	90.2
15.....	1:1	57.1	81.2	2.6	42.9	3.3	51.2	4.6	5.8	10.4	89.6

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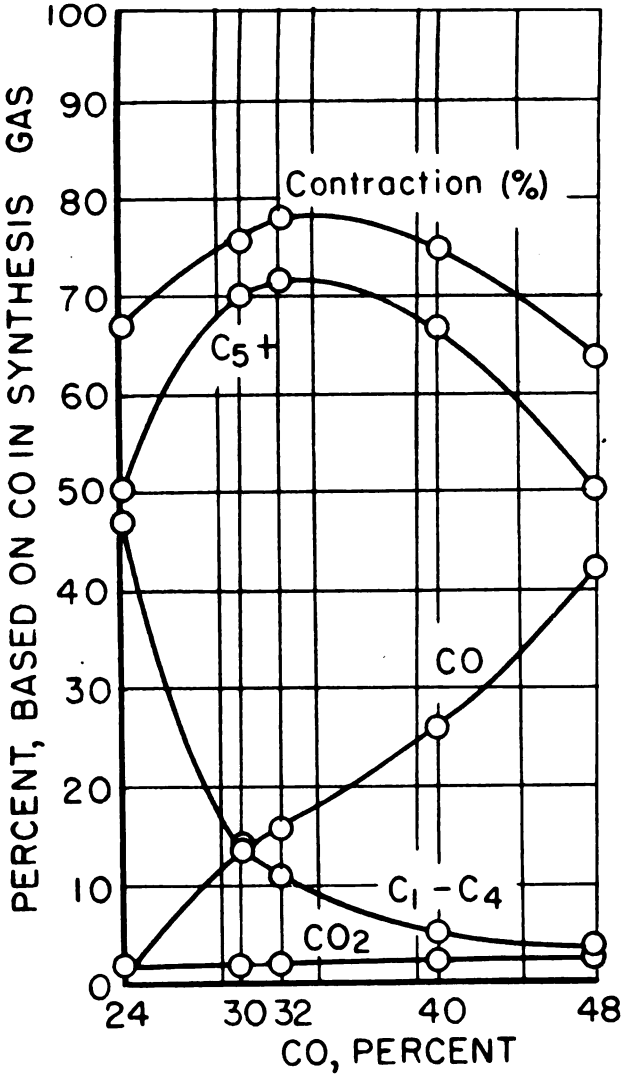

Figure 7.– Effect of synthesis gas composition on hydrocarbon synthesis

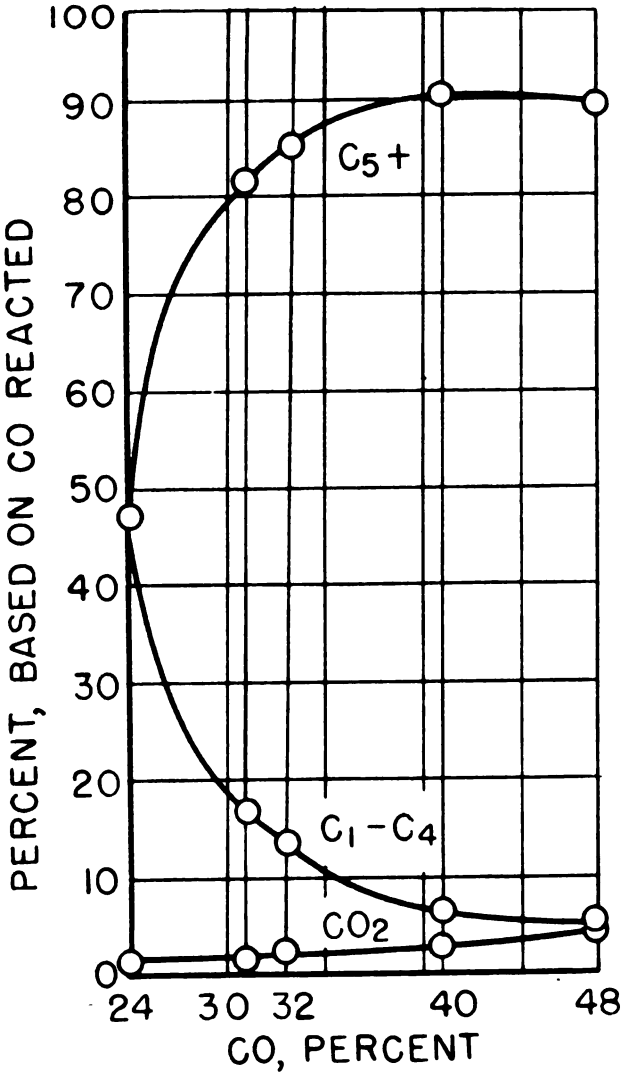

Figure 8.–Effect of synthesis gas composition on hydrocarbon synthesis

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The results in table 6 are shown graphically in figures 7 and 8. The experimental results shown in these figures may be summarized as follows: (A) The yield of liquid hydrocarbons based on carbon monoxide in the synthesis gas was a maximum (143.7 ml./m.^{3}) at an H_2:CO ratio of 2:1; at an H_2:CO ration of 3:1, a satisfactory yield of liquid hydrocarbons was obtained only when the reaction temperature was lowered to 180° C. (B) At an H_2:CO ratio of 3:1, the carbon monoxide conversion is a maximum, and at 200° C. it is nearly quantitative; the carbon monoxide conversion decreases as the H_2:CO ratio decreases from this value. In contrast to the behaviour of carbon monoxide, the conversion of hydrogen exhibits a maximum at an H_2:CO ratio of 2:1, (C) The conversion of carbon monoxide to carbon dioxide increases with decreasing H_2:CO ratio, whereas the conversion to gaseous paraffins decreases. (D) Based on the carbon monoxide reacted, the conversion of carbon monoxide to carbon dioxide increases with decreasing H_2:CO ratio; although similar conversion to liquid hydrocarbons also increases with decreasing H_2:CO ratio, a maximum is exhibited at an H_2:CO ratio of 1.5:1.

Discussion

By computing from table 5 the yield of liquid hydrocarbons per cubic meter of carbon monoxide in the synthesis gas, the following results are obtained:

Experiment No.	H_2:CO	Reaction temperature, °C.	Liquid hydrocarbons	
			ml./m.3 of CO in synthesis gas	ml./m.3 of synthesis gas
11A.....	3:1	180	446.2	112
11B.....	3:1	190	314.9	79
11C.....	3:1	200	217.9	54
12.....	2.5:1	200	461.9	132
13.....	2:1	200	443.5	148
14.....	1.5:1	200	342.0	137
15.....	1:1	200	219.5	110

These computations showed a maximum yield of liquid hydrocarbons per cubic meter of carbon monoxide in the synthesis gas at an H_2:CO ratio of 2.5:1; thus, in order to most effectively utilize carbon monoxide, an excess of two to three times as much hydrogen is necessary. It is also evident from these calculations that at an H_2:CO ratio of 3:1, lowering the reaction temperature 20° C. below that used at an H_2:CO ratio of 2:1 yield comparable amounts of liquid hydrocarbons.

STUDIES OF CATALYSTS FOR THE HYDROCARBON SYNTHESIS

As catalysts for this reaction, Fischer and Tropsch[27] first used iron compounds. However, iron catalysts produce carbon dioxide during the reaction, complicating utilization of the unreacted gases, and, thus, nickel or cobalt catalysts have been used more recently. According to Fischer and Koch,[28] the general equations for these catalytic reactions are:

27/ Work cited in footnote 6.

28/ Fischer, F., and Koch, H., [The Chemistry of the Hydrocarbon Synthesis and General Properties of the Resulting Products (Gasol, Gasoline, Diesel Oil, and Paraffin Waxes)] : Brennstoff Chem., vol. 13, No. 22, Nov. 15, 1932, pp. 428-434.

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In the case of iron catalysts:

(a) $2nCO + nH_2 \longrightarrow C_nH_{2n} + nCO_2$

(b) $2nCO + (n+1)H_2 \longrightarrow C_nH_{2n+2} + nCO_2$

In the case of nickel or cobalt catalysts:

(a) $nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$

(b) $nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$.

In other words, with iron catalysts the reaction is characterized by the production of carbon dioxide, whereas, with nickel or cobalt catalysts water is produced. Oxygen liberated when the carbon monoxide combines with iron, nickel, or cobalt (to produce their respective carbides) reacts with other carbon monoxide, in the case of iron catalyst, to produce carbon dioxide, and with hydrogen, in the case of nickel or cobalt catalyst, to produce water. Because of the inexpensiveness of iron catalysts as compared with nickel or cobalt catalysts, the development of an iron catalyst with an activity as high as that of nickel or cobalt catalysts would be highly desirable industrially. This problem will be treated in a later report; investigations involving nickel, cobalt, or nickel-cobalt mixed catalysts are reported here.

A synthesis of this type, as explained previously, is most advantageously carried out at low reaction temperatures. Hence, it is necessary that a catalyst of the greatest possible activity be utilized in order to operate in the desired low-temperature range. It is a generally accepted fact that catalysts that are prepared by precipitation have a much higher activity than those obtained by calcination of mixed salts of the catalyst components. Thus, Fischer and Meyer29/ and Fischer and Koch30/ used a catalyst that was obtained by precipitation with alkali from mixed nitrate salt solution and succeeded in lowering the reaction temperature to approximately 200° C. The activity of a precipitated catalyst, however, is greatly affected by the type of precipitant, the method of precipitation, and the method of removing electrolytes. For example, when such precipitants as ammonia and ammonium carbonate are used, there is no electrolyte-removal problem; when alkali is used, quantitative removal of the adsorbed precipitant is virtually impossible, no matter how carefully the precipitate is washed. The minute quantities of precipitant thus remaining may have a material effect upon the activity of the catalyst; accordingly, the selection of precipitant is vital. Fischer established alkaline carbonates as the best precipitants for nickel or cobalt catalysts, considering it most effective to have a quantity of alkaline carbonate remain after washing the precipitate with a constant amount of water. This method of controlling the amount of alkaline carbonate in the catalyst is subject to considerable difficulty; a more satisfactory method is to add a constant quantity of alkaline carbonate to the precipitate after it has been thoroughly water washed, as done by Fujimura and Tsuneoka.31/

29/ Work cited in footnote 12.

30/ Work cited in footnote 13.

31/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XIII and XIV. Nickel Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 36, 1933, p. 379; supplemental binding pp. 119-121; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 242-253.

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Effects of the Carrier

It has been widely acknowledged that the effectiveness of hydrogenation catalysts, such as nickel, cobalt, and iron, is remarkably promoted by the use of inorganic carriers, such as diatomaceous earth, pumice, and asbestos. Of great significance from economic considerations is the fact that in the hydrocarbon synthesis the presence of a suitable carrier enhances both the reaction rate and the yield of liquid hydrocarbons. Fischer[32] considered the "stuttgarter masse" (artificial stone made of granular quartz and water glass) the most suitable carrier for Co-Cu catalysts. For Co-Cu-MgO catalysts, Fujimura[33] used 200-mesh powdered or 3-mm. granular pumice as a carrier and added cane sugar along with the nitrate salts during the preparation of the catalyst; the calcined catalyst produced an increased yield of liquid hydrocarbons.

Fischer and Meyer[34] and Fischer and Koch[35] found diatomaceous earth superior as a carrier for precipitated nickel or cobalt catalysts. These workers considered a low bulk density as highly desirable in a carrier and utilized an air-separated material from one locality with a bulk density of about 0.1. A comparison of this material with Merck diatomaceous earth having a bulk density of 0.0337 shows the yield of liquid hydrocarbons in the latter case was only one-fifth of the former. Magnesia was found to be unsuitable as a carrier. The most suitable ratio between metal and diatomaceous earth was determined as 1:1 for nickel catalysts and 1:1.5 for cobalt catalysts. Fujimura[36] used 10 to 12 gm. of diatomaceous earth per 3 gm. of cobalt as a carrier for cobalt-copper catalysts and added starch along with the nitrate salts; an increased yield of liquid hydrocarbons was obtained. Fischer and Meyer[37] used silica or graphite with good heat-conducting properties rather than diatomaceous earth; calcium carbonate, or basic magnesium carbonate in Ni-Mn-Al_2O_3 catalysts but did not obtain satisfactory results.

Amount of Carrier

By using a 100 Co:5 Cu:12 U_3O_8 catalyst corresponding to 3 gm. of cobalt and by varying the cobalt:diatomaceous earth ratio utilizing 72.0 l. of synthesis gas in each case, the results listed in table 7 were obtained.

32/ Work cited in footnote 21.

33/ Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure IX. Additional Tests with a Cobalt-Copper-Magnesium Oxide Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 1005; supplemental binding No. 7, pp. 227-229.

34/ Work cited in footnote 12.

35/ Work cited in footnote 3.

36/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XI. Cobalt-Copper-Thorium and Cobalt-Copper-Uranium Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 35, 1932, p. 532; supplemental binding pp. 179-182; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 189-197.

37/ Fischer, F., and Meyer, K., [Effect of Preparation Conditions on the Activity of Nickel-Manganese-Aluminum Catalysts]: Brennstoff Chem., vol. 14, No. 3, Feb. 1, 1933, pp. 47-50.

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TABLE 7. - Effect of carrier

(Gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment number	Cobalt: kieselguhr ratio	Temperature, °C.	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./m.³ of synthesis gas		Product gas composition, percent						
			CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
16.....	3:1	200	32.8	65.0	2.2	78.8	122.7	190.4	7.8	0.2	19.8	46.2	16.9	1.36	9.1
17.....	2:1	200	32.2	65.6	2.2	80.4	120.8	200.0	7.2	.1	24.7	40.1	16.2	1.37	11.7
18A.....	1:1	190	32.5	64.8	2.7	75.4	133.3	179.2	2.0	-	20.0	57.7	10.3	1.53	10.0
18B.....	1:1	200	32.8	65.0	2.2	80.6	143.3	193.7	4.6	.2	23.4	43.8	16.5	1.31	11.5
19A.....	3:4	190	32.8	64.9	2.3	78.5	143.0	198.5	2.0	.1	24.0	52.2	11.8	1.52	9.9
19B.....	3:4	200	32.5	65.0	2.5	80.6	140.5	206.6	4.4	-	25.4	44.5	12.8	1.31	12.9

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In the usual manner, the carbon monoxide and hydrogen conversions were obtained from a knowledge of the gas contraction and the analyses of the synthesis and product gases; the percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons were then calculated on the basis of the carbon monoxide in the synthesis gas, and their sum was subtracted from 100, the difference being the percentage of carbon monoxide converted into gasoline (C_{5+}). These results are given in table 8. From these tables it is evident that as the diatomaceous earth content of the catalyst is increased, the yield of gasoline also is increased and passes through a maximum at a metal:carrier ratio of 1:1 or 3:4. However, table 8 shows that the carbon monoxide conversion was about the same at all ratios, and that the increase or decrease in the yield of gasoline (C_{5+}) was governed by the quantities of carbon dioxide and gaseous saturated hydrocarbons produced. As the production of carbon dioxide and gaseous saturated hydrocarbons is accelerated with increase in temperature at high metal:carrier ratios, the temperature of the catalyst itself may be considered to be increased. That is, at a cobalt:diatomaceous earth ratio of 3:1, if reaction starts at a given point the heat of reaction can easily be transmitted through a small quantity of diatomaceous earth and activate the adjacent active center. In this manner, the heat of reaction is propagated throughout the catalyst mass, and the reaction takes place at a large number of the active centers. Hence, the temperature of the catalyst is raised by the heat of the reaction, and the production of carbon dioxide and gaseous saturated hydrocarbons is accelerated. At cobalt:diatomaceous earth ratios of 3:4 or 1:1, the heat of reaction generated at a given active center is transmitted to the diatomaceous earth, but, as the quantity of diatomaceous earth is large, less energy is received by the adjacent active center, and the resulting activation is correspondingly smaller. Therefore, the production of carbon dioxide and gaseous saturated hydrocarbons is likewise smaller.

On the basis of these considerations, it is postulated that in this reaction the number of active centers at cobalt:diatomaceous earth ratios of 3:4 or 1:1 is sufficient for the synthesis, and at ratios of 3:1 or 2:1 there are more than the necessary number of active centers.

Type of Carrier

The effect of carriers other than diatomaceous earth is shown in table 9. A weight ratio of 1:1 of cobalt to pumice, kaolin, or silica gel was used. The catalyst sample contained 3 gm. of cobalt in a composition of 100 Co:5 Cu:12 U_3O_8.

Experiment 20. - Unrefined commercial kaolin was used, and the production of carbon dioxide and gaseous saturated hydrocarbons was much larger than that of experiment 18, in which diatomaceous earth was used.

Experiment 21. - Granular pumice was pulverized to 120-mesh. It was then boiled for several hours with concentrated nitric acid to remove the iron particles. After thorough water washing and drying at about 120° C., the pumice was ready to use. The volume of carbon dioxide and gaseous saturated hydrocarbons in the product gas was generally similar to that obtained when kaolin was used.

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TABLE 8. - Effect of carrier

Experiment No.	CO conversion, percent	H_2 conversion, percent	Carbon distribution: Percent of CO in synthesis gas: CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})	Percent of CO reacted: CO_2	C_nH_{2n+2} (C_1-C_4)	$CO_2+C_nH_{2n+2}$	Gasoline (C_{5+})
16.....	87.3	84.9	5.0	12.7	14.8	67.5	5.7	17.0	22.7	77.3
17.....	85.0	88.0	4.4	15.0	13.5	67.1	5.2	15.9	21.1	78.9
18A.....	84.9	78.1	1.5	15.1	11.9	71.5	1.8	14.0	15.8	84.2
18B.....	86.2	86.9	2.7	13.8	12.8	70.7	3.1	14.8	17.9	82.1
19A.....	84.3	82.7	1.3	15.7	11.8	71.2	1.5	14.0	15.5	84.5
19B.....	84.8	86.7	2.6	15.2	10.1	72.1	3.1	11.9	15.0	85.0

TABLE 9. - Effect of carrier

(Catalyst = 100 Co:5 Cu:12 U_3O_8; gas velocity = 6 l./hr.; 72.0 l. synthesis gas used in each case.)

Experiment No.	Carrier	Reaction temperature, °C.	Composition of synthesis gas, percent: CO	H_2	N_2	Contraction, percent	Liquid products, ml./m^3 of synthesis gas: Gasoline (C_{5+})	Water	Product gas composition, percent: CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
20.....	Kaolin	200	31.6	65.0	3.4	78.0	112.5	187.9	9.6	0.4	12.2	40.1	22.2	1.64	15.5
21.....	Pumice	200	33.0	64.2	2.8	76.8	116.6	195.8	7.8	.2	14.0	43.8	22.9	1.20	11.3
22.....	Silica gel	210	32.8	64.0	3.2	76.3	125.0	175.0	4.6	-	19.0	54.0	9.0	1.30	13.4

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Experiment 22. - Unrefined silica gel was used, which was salt-free and very voluminous and which had been obtained from Dr. Altpeter and Dr. Richter, Chemiches Laboratorium. At 200° C., unfavorable yields of liquid hydrocarbons and poor gas contractions were obtained, and it was necessary to raise the temperature to 210° C. This catalyst was the least active of the three tested in this group.

From tables 7 and 9, it is evident that the yield of gasoline (C_{5+}) is considerably smaller when kaolin, pumice, or silica gel was the carrier than when diatomaceous earth was used. Correspondingly, large amounts of carbon dioxide and gaseous saturated hydrocarbons were produced when pumice and kaolin were used. In view of the results obtained with diatomaceous earth, which suggested that decreasing amounts of carrier produced increasing catalyst temperatures (as indicated by the increased production of carbon dioxide and gaseous saturated hydrocarbons), the necessity of raising the operating temperature to obtain a significant yield of liquid hydrocarbons in the silica-gel experiment may be attributed to the presence of an excessive quantity of carrier. As the bulk densities of pumice and kaolin are four times greater than that of diatomaceous earth, weights of these materials four times that of diatomaceous earth would have to be used to obtain an equivalent volume of carrier in each case. Conversely, the bulk density of silica gel is half that of diatomaceous earth, and a weight of silica gel equal to only half the weight of the diatomaceous earth would be needed. These relationships are shown in the following table 10.

TABLE 10. - Relationship of carrier bulk densities

Carrier	Volume of 3 gm. of carrier, ml.	Weight of carrier equivalent in volume to 3 gm. of diatomaceous earth	Bulk density gm./ml.
Diatomaceous earth.....	17	3	0.18
Pumice.....	4	13	.75
Kaolin.....	4	13	.75
Silica gel.....	34	1.5	.09

Studies of the effects of the carrier were then undertaken on the basis of a constant volume rather than a constant weight. Experimental results obtained by incorporating in the catalyst (100 Co:5 Cu:12 U_3O_8, weight of cobalt = 3 gm.) quantities of pumice, kaolin, and silica gel, respectively, corresponding to 17 ml. of diatomaceous earth are shown in table 11.

Experiment 23. - Using Kaolin at 200° C., neither favorable gas contraction nor gasoline (C_{5+}) yield was indicated, and it was necessary to raise the temperature to 210° C. On comparing this experiment with experiment 20, it is evident that the volumes of carbon dioxide and gaseous saturated hydrocarbons in the product gases were reduced, but because the gas contraction was reduced at the same time, the yields of gasoline were approximately the same in both experiments. In experiment 23, extremely rapid deterioration in catalyst activity was observed.

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TABLE 11. - Effects of the carrier

(100 Co:5 Cu:12 U_3O_8 catalyst; reaction temperature = 210° C.; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Carrier	Weight, gm.	Composition of synthesis gas, percent			Contraction, percent	Liquid products, ml./$m.^3$ of synthesis gas		Product gas composition, percent						
			CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_mH_{2n+2}	n	N_2
23.....	Kaolin	13	33.0	63.8	3.2	70.5	114.2	178.0	2.0	0.2	29.0	57.5	5.2	1.32	6.1
24.....	Pumice	13	33.8	64.0	2.2	71.2	115.6	175.0	3.0	.4	28.2	54.0	7.2	1.40	7.2
25.....	Silica gel	1.5	32.8	64.8	2.4	77.6	128.2	193.7	6.0	-	26.4	45.0	13.4	1.22	9.2

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Experiment 24. - In this experiment, in which pumice was used, it was necessary, as in experiment 23, to increase the temperature to 210° C., and the yield of gasoline (C_{5+}) was not greatly different here from that of experiment 21, in which 3 gm. of pumice was used. Signs of low catalyst durability also were observed.

Experiment 25. - Although half the weight of silica gel previously used was employed in this experiment, the reaction temperature could not be lowered; 210° C. was still the most suitable operating temperature. The gas contraction was somewhat greater here, but, as the production of carbon dioxide and gaseous saturated hydrocarbons also was increased, only a very small increase resulted in the yield of gasoline. In this experiment, however, the durability of the catalyst was found to be high, as in the case of diatomaceous earth.

These results indicate that kaolin, pumice, and silica gel are inferior to diatomaceous earth as carriers. With respect to bulk density, it is . . . believed that the larger the bulk volume per unit weight, the better the . . . results. However, although the bulk density of silica gel is one half that of diatomaceous earth, its function as a carrier is inferior to diatomaceous earth. The explanation for this apparently contradictory behaviour may lie in the role the carrier may play as a simple carrier as well as the part played by its binding properties. As the bulk densities of kaolin and pumice were equal, and as similar results were obtained in each case, no violent poisoning action can be attributed to the alumina in the kaolin as described by Fischer and Koch.38/

Effects of Raw Materials Used in Catalyst Preparation

The effects of the raw materials used in preparing the catalyst were determined by preparing 100 Co:5 Cu:12 U_3O_8 catalyst from cobalt sulfate, cobalt chloride, cobalt nitrate, and cobalt acetate solutions. The activities of the resulting catalysts are compared in table 12. The salt solutions were prepared as described in the Experimental section, and the precipitates were obtained by the addition of potassium carbonate solution. The precipitates then were thoroughly water-washed to minimize the remaining sulfate, chloride, nitrate, and acetate salts. The results obtained for cobalt nitrates in experiments 18A and B are listed again for convenience in comparison.

Experiments 26A and B. - In this experiment, cobalt sulfate (Kato, guaranteed) was used. The catalyst was first reduced in hydrogen at 250° C. for 1 hour. Then the flow of synthesis gas was started, and, at 210° C., 60.4 ml. of gasoline (C_{5+}) was obtained per cubic meter of synthesis gas. This yield increased to 81.2 ml./m^3 at 220° C., an activity considerably less than that exhibited in experiment 18A, in which nitrate salts were used. The cause for this decreased activity may be linked with the potassium sulfate produced by the reaction between cobalt sulfate and potassium carbonate. If the potassium sulfate is not adequately removed by water washing, the remainder may be absorbed into the precipitate and exert a subsequent poisoning effect on the catalyst. As residual potassium nitrate seems to exert no poisoning effect, the poisoning action of potassium sulfate may be presumed to be due to the action of negative $SO_4^=$ ions.

38/ Work cited in footnote 3.

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TABLE 12. - Effects of raw materials from which catalyst is prepared

(100 Co:5 Cu:12 U_3O_8 catalyst equivalent to 3 gm. of Co; gas velocity = 6 l./hr.)

Experiment No.	Raw material	Reaction temperature, °C.	Amount of gas used, liters	Gas contraction, percent	Liquid products, ml./m.^{3}	
					Gasoline (C_{5+})	Water
26A.....	Sulfate	210	56.0	48.5	60.4	83.3
26B.....	Sulfate	220	56.0	53.4	81.2	108.3
27.....	Chloride	210	36.0	0	0	0
18A.....	Nitrate	190	72.0	75.4	133.3	179.2
18B.....	Nitrate	200	72.0	80.6	143.3	193.7
28A.....	Acetate	190	72.0	76.8	130.5	185.0
28B.....	Acetate	200	72.0	81.5	145.2	200.0

Experiment 27. - In this experiment, cobalt chloride (Kato, guaranteed) was used. In spite of reduction in hydrogen for 1 hour at 250° C., no signs of activity were found at operating temperatures up to 220° C. A violent poisoning effect on this catalyst is thus exhibited by Cl^-.

Experiment 28A and B. - In this experiment, cobalt acetate (Kato, pure) was used. After hydrogen reduction at 200° C. for 1 hour, the flow of synthesis gas was started. At 190° and 200° C., 130.5 ml. and 145.2 ml. of gasoline (C_{5+}), respectively, were produced per cubic meter of synthesis gas; this activity is virtually the same as that obtained in catalysts prepared from nitrate salts. As CH_3COO^- exerts no poisoning effect on the final catalyst, cobalt acetate, like cobalt nitrate, may be used effectively as a raw material in catalyst preparation.

Nickel Catalyst

The production of methane by hydrogenation of carbon monoxide over reduced nickel was first investigated by Sabatier and Senderens[39] in 1902. According to these investigators, the hydrogenation of carbon monoxide commences at 180° to 200° C. when reduced nickel is used, and a steady production of methane is obtained at 230° to 250° C. Orlov[40] reduced carbon monoxide over asbestos impregnated with nickel and palladium and found that unsaturated compounds were produced at a comparatively low temperature (100° C.). Medsforth,[41] in his investigation of the production of methane, added various difficulty reducible metal oxides to reduced nickel on the theory that as the reduction of carbon monoxide to methane entailed a dehydrating reaction it was desirable to use these oxides, which are known to be dehydrating catalysts. Metallic oxides were found to be decreasingly effective in promoting this reaction, in the following order: CeO_2, ThO_2, GeO, Cr_2O_3, Al_2O_3, SiO_2, and ZrO_2. Russell and

39/ Sabatier, P., and Senderens: Compt. rend., vol. 134, 1902, p. 514.
40/ Orlov, G., Jour. Russian Phys. Chem., vol. 40, 1909, p. 1588.
41/ Medsforth, S., Promotion of Catalytic Reactions I: Jour. Chem. Soc., vol. 123, 1923, pp. 1452-1469.

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Taylor[42] studied the absorption action of reduced nickel in the reaction $CO_2+4H_2 \longrightarrow CH_4+2H_2O$, and found that when a small quantity of thoria was added to the reduced nickel the over-all reaction rate was increased 10 times, but the increase in the absorption rate was only several tenths of a percent. They inferred from this that absorption and catalytic activity were not directly related. Fischer and Tropsch[43] and Elvins[44] predicted that, as nickel had excellent hydrogenation properties, methane would be produced with ease, but that the production of high-boiling liquid hydrocarbons would be difficult. However, Fischer and Meyer[45] succeeded in preparing a highly practical nickel catalyst for gasoline (C_{5+}) production and have increased this yield remarkably by lowering the reaction temperature to about 200° C.

In this country, Fujimura and Tsuneoka[46] of Kyoto Imperial University studied nickel catalysts. They observed the effect of adding alkali carbonates to nickel-manganese and nickel-thoria catalysts and of adding various promoters to nickel-manganese catalysts.

Experimental Procedure

Catalyst. - To a nickel nitrate solution corresponding to 3 gm. of nickel was added a solution containing a fixed percentage (with regard to nickel) of nitrates of manganese, cerium, alumina, or thoria. An appropriate amount of diatomaceous earth was then added, followed by an amount of potassium carbonate slightly in excess of the stoichiometric equivalent. The precipitate was filtered and dried on a water bath. It was then spread in a layer in the 24-centimeter-long constant-temperature zone of the reaction tube and reduced in hydrogen for 4 to 5 hours at a temperature of 350° to 450° C. When uranium oxide, tungsten oxide, or silica gel was used as a promoter, nickel and manganese carbonates were precipitated on the diatomaceous earth. Uranium oxide was then added by precipitating the nitrate with ammonia; tungsten oxide was added as the oxide obtained by dissolving the ammonium salt with concentrated nitric acid; and the silica gel was added after having been boiled with distilled water for 2 to 3 hours and dried at about 120° C.

Synthesis gas. - $CO:H_2 = 1:2$ was used.

Results

(A) Nickel-manganese catalysts. - Fischer and Meyer[47] considered a manganese content of 15 to 20 percent that of nickel as most suitable while Fujimura and Tsuneoka[48] considered 15 percent the optimum. These variations in results

42/ Russell, W. W., and Taylor, H. S., The Promoter Action of Thoria on Nickel Catalysts: Jour. Phys. Chem., vol. 29, 1925, pp. 1325-1341.
43/ Work cited in footnote 6.
44/ Work cited in footnote 22.
45/ Work cited in footnote 12.
46/ Work cited in footnote 31.
47/ Work cited in footnote 12.
48/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XV and XVI. Nickel Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 36, 1933, p. 999; supplemental binding pp. 413-416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 254-263.

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may be attributed to differences in manufacturing conditions and carrier properties. Results obtained at manganese contents of 12, 16, and 20 percent, respectively, are shown in table 13.

TABLE 13. - Nickel-manganese catalysts; effect of manganese content

(3 gm. of Ni + 3 gm. of diatomaceous earth; gas velocity = 6 l./hr.)

Experiment No.	Composition of catalyst	Reaction temperature, °C.	Volume gas used, liters	Gas contraction, percent	Liquid products, ml./m.^{3}	
					Gasoline (C_{5+})	Water
29.....	Ni + 12% Mn	205	72.0	58.0	65.3	135.6
30.....	Ni + 16% Mn	205	72.0	70.5	100.0	152.8
31A.....	Ni + 20% Mn	200	36.0	68.5	92.3	148.5
31B.....	Ni + 20% Mn	205	72.0	72.5	107.6	160.6

A manganese content of 20 percent was found to be the optimum, producing a yield of liquid hydrocarbons, equal to 107.6 ml./m.^{3} of synthesis gas. When hydrogen peroxide was added to a solution of nickel and manganese nitrates, and manganese dioxide was precipitated to produce a catalyst containing 20 percent manganese, no change was obtained in the liquid hydrocarbon yield. A reaction temperature of 205° C. produced a better gasoline yield than a temperature of 200° C. although an increase in the reaction temperature is usually associated with an increased production of gaseous saturated hydrocarbons and a reduction in the yield of liquid hydrocarbons. The results obtained on reducing the quantity of diatomaceous earth from 3 gm. of 2.5, 2, and 1.5 gm. in an attempt to lower the reaction temperature are shown in table 14.

TABLE 14. - Nickel-manganese catalysts; effect of carrier content

(3.0 gm. Ni + 0.6 gm. Mn; gas velocity = 6 l./hr.;
72.0 l. of synthesis gas used in each case)

Experiment No.	Diatomaceous earth, gm.	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m.^{3}	
				Gasoline (C_{5+})	Water
32.....	2.5	200	73.4	114.0	160.0
32A.....	2.0	200	75.0	120.5	170.6
32B.....	2.0	205	75.8	108.0	175.0
34.....	1.5	200	75.0	118.0	170.5

Although a slight increase in gas contraction was observed with smaller quantities of diatomaceous earth, no material difference was evident in the activities of the three catalysts. The largest yield of gasoline (C_{5+}) was obtained at a carrier content of 2.0 gm., and a temperature of 200° C. was found to be more favorable than 205° C.

The effects of adding 4 percent (based on nickel) of uranium oxide, cerium oxide, alumina, or tungsten oxide to a catalyst containing Ni + 20 percent Mn + 66 percent diatomaceous earth are shown in table 15.

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TABLE 15. - Nickel-manganese catalysts; effect of promoters

(100 Ni:20 Mn:4 promoter:66 diatomaceous earth; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Promoter	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m.3	
				Gasoline (C_{5+})	Water
35.....	U_3O_8	190	78.4	138.5	185.2
36.....	CeO_2	200	72.5	125.0	178.5
37.....	Al_2O_3	200	74.2	132.6	180.5
38.....	WO_3	200	71.8	128.0	188.0

Experiment No. 35. - Fujimura and Tsuneoka[49] had found previously that uranium oxide was effective as a promoter for nickel. In the catalysts in the present experiments, nickel and manganese were precipitated as carbonates by potassium carbonate, and to this was added ammonium uraniumate, obtained by adding ammonia to uranium nitrate. The catalyst thus prepared showed a considerably greater activity than Ni + 20 percent Mn, for the reaction temperature, 190° C., was 10° lower.

Experiment No. 36. - Cerium oxide was used by Erdley and Nash[50] and Kodama[51] as a promoter for cobalt-copper catalysts, but it had never been tried on nickel. Accordingly, such a catalyst was prepared by precipitating the cerium along with nickel and manganese as the carbonates by potassium carbonate. Only a slight increase in activity was exhibited, however, over that of Ni + 20 percent Mn catalyst. Cerium oxide is not an effective promoter, therefore, for this type of catalyst.

Experiment No. 37. - Fischer and Meyer[52] and Fujimura and Tsuneoka[53] reported that alumina was a superior promoter for nickel-manganese catalysts. Therefore, nickel and manganese were precipitated as the carbonate salts by potassium carbonate, and a definite amount of alumina was added by treating an aluminum nitrate solution with ammonia. The resulting preparation showed a superior gas contraction and gasoline (C_{5+}) yield.

Experiment No. 38. - A catalyst was prepared by adding tungsten oxide, obtained by dissolving ammonium tungstate in concentrated nitric acid, to mixed carbonate salts of nickel and manganese. The promoting action of tungsten oxide was similar to that of cerium oxide, for the resulting activity was low.

Various combinations of the effective promoters, uranium oxide and alumina, were next tried with the results shown in table 16.

49/ Work cited in footnote 31.
50/ Work cited in footnote 7.
51/ Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure V. The Influence of Titanium Oxide, Zirconium Oxide, and Cerium Oxide]: Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 620; supplemental binding (in German), pp. 202-203: Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, Nos. 257-259, 1930, pp. 13-25.
52/ Work cited in footnote 12.
53/ Work cited in footnote 48.

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TABLE 16. - Nickel-manganese catalysts; effect of promoters

(Ni + 20% Mn catalyst equivalent to 4 gm. of nickel; reaction temperature = 200° C.; gas velocity = 6 l./hr.)

Experiment No.	Promoter percent	Volume gas used, l.	Gas contraction, percent	Liquid products, ml./m.^{3}	
				Gasoline (C_{5+})	Water
39A[a].....	8 U_3O_8	72.0	84.8	152.0	218.5
39B1.....	8 U_3O_8	72.0	85.0	150.5	216.0
39B2.....	8 U_3O_8	72.0	88.2	159.0	218.5
39B3.....	8 U_3O_8	72.0	86.6	158.2	210.0
39B4.....	8 U_3O_8	72.0	86.2	154.0	208.2
39B5.....	8 U_3O_8	72.0	86.5	154.2	208.0
39C.....	8 U_3O_8	360.0	86.5	155.2	212.1
40[a].....	8 Al_2O_3	72.0	73.2	118.6	169.0
41.....	8 U_3O_8 4 Al_2O_3	216.0	84.8	166.5	220.0
42.....	8 U_3O_8 4 WO_3	216.0	84.2	162.3	218.5
43.....	8 U_3O_8 4 ThO_2	216.0	87.8	168.8	226.0
44.....	10 Silica gel	72.0	74.5	122.6	175.0

a/ Catalyst equivalent to 3 gm. of nickel used.

Experiment Nos. 39A, B, and C. - Ni + 20 percent Mn + 8 percent U_3O_8 catalyst corresponding to 3 gm. of nickel was used in experiment 39A. The nickel content was then increased from 3 to 4 gm. to test the durability of the catalyst. Five tests, designated as experiment 39B-1, 2, 3, 4, and 5, were made with 72.0 l. of synthesis gas for each. In the first test the yield of gasoline (150.5 ml./m.^{3}) was comparatively low, considering the large gas contraction, a result of the large production of gaseous hydrocarbons. The production of gasoline then increased to 159.0 ml. per cubic meter of synthesis gas in the second test and decreased in the remaining tests, resulting in an average value for the 360.0 l. of synthesis gas of 155.2 ml./m.^{3} (experiment 39C).

Upon completion of each separate experiment, the synthesis gas in the reaction tube was displaced by hydrogen; therefore, the carbon and the high-boiling hydrocarbons deposited on the catalyst, which may cause the catalyst to deteriorate, may have reacted to some extent with the hydrogen and in this manner may have been removed from the reaction tube. Hence, it is possible that the catalyst may have been partly reactivated. Because hydrogen is known to diffuse through rubber tubing, and because of the contraction of the cooled gases, the internal pressure was decreased, and it is probable that a small amount of air was taken into the system. Consequently, possible oxidation from this source must also be considered. Operation on a continuous basis over a prolonged period to study the true durability of the catalyst will be discussed elsewhere.

Experiment No. 40. - Increasing the alumina content from 4 to 8 percent reduced the activity considerably; 118.6 ml. of gasoline was obtained, compared to the previous yield of 132.6 ml./m.^{3} of synthesis gas.

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Experiment Nos. 41 to 43. - Eight percent uranium oxide has been shown to be the best promoter for Ni + 20 percent Mn catalyst. In an attempt to activate the catalyst composition still further, 4 percent of alumina, tungsten oxide, or thoria was added to Ni + 20 percent Mn + 8 percent U_3O_8 catalyst (corresponding to 4 gm. of nickel). These materials proved decreasingly effective in the order: thoria, alumina, and tungsten oxide, producing 168.8, 166.5, and 162.3 ml. of gasoline per cubic meter of synthesis gas, respectively.

Experiment No. 44. - According to Brückner and Jacobus,[54] if 10 percent silica gel is added to nickel, the production of methane by catalytic hydrogenation of carbon monoxide is increased about 2.5 times, and the durability of the catalyst is increased significantly. However, in this experiment, when silica gel corresponding to 10 percent of nickel was added to Ni + 20 percent Mn catalyst, activity was increased only slightly.

(B) Nickel-uranium oxide catalysts. - Fujimura and Tsuneoka[55] showed that uranium oxide was effective as a promoter for nickel; these workers used ammonium carbonate as a precipitant for nickel in preparing the catalyst. By using potassium carbonate, however, a very effective catalyst was prepared in this laboratory. The results obtained by adding 18, 16, and 12 percent, respectively, of uranium oxide to nickel are shown in table 17.

TABLE 17. - Nickel-uranium oxide catalysts

(Catalyst contained 3 gm. Ni; gas velocity = 6 l./hr.; volume gas used in each test = 72.0 l.)

Experiment No.	U_3O_8 content, percent of Ni in catalyst	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m.³	
				Gasoline (C_{5+})	Water
45A.....	18	180	88.6	144.8	188.2
45B.....	18	180	82.2	137.0	190.4
45C.....	18	185	88.0	148.0	198.0
45D.....	18	185-190	88.8	136.5	207.4
Average	18	180-190	86.9	141.6	196.0
46.....	16	190	78.5	137.5	202.3
47.....	12	190	76.8	135.8	189.0

Experiment No. 45. - This catalyst, nickel to which 18 percent uranium oxide had been added, showed extremely high activity during the first part of the experiment but deteriorated rapidly. At 180° C., a gas contraction of about 94 percent was indicated during the first 2 to 3 hours, but after 12 hours the contraction decreased to 82 percent; 144.8 ml. of gasoline (C_{5+}) per cubic meter of synthesis gas was produced during this period. In this case, the ratio between the relatively heavy oil condensed in the burette, and the light oil absorbed by the activated carbon was 2.5:1. In addition, a small quantity of solid paraffin was deposited at the exit of the reaction tube during the last phase of the reaction, and this suggests a reason for the rapid

54/ Brückner, H., and Jacobus, G., [The Activity of Nickel Catalysts in the Methane Synthesis]: Brennstoff Chem., vol. 14, 1933, pp. 265-268.
55/ Work cited in footnote 31.

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deterioration in catalyst activity. In experiment 45B, although the reaction proceeded at 180° C., the gas contraction decreased from 88.6 percent to 82.2 percent and the yield of gasoline from 144.8 to 137.0 ml./m.^{3} of synthesis gas. Similarly, the reaction temperature had to be increased continuously in experiments 45C and D in order to maintain a suitable gas contraction. As a considerable quantity of solid paraffin had been deposited at the exit of the reaction tube when experiment 45 was concluded, the amount of uranium oxide was reduced from 18 percent to 16 percent to prevent formation of excessive amounts of high-molecular-weight hydrocarbons in future experiments.

Experiment No. 46. - Although the decrease in uranium oxide content succeeded in reducing the ratio of the production of relatively heavy oil to light oil from 2.5:1 to 1.8:1, a small quantity of solid paraffin was still found at the end of the reaction tube at the conclusion of this experiment.

Experiment No. 47. - The uranium oxide content was decreased still farther, to 12 percent, and a heavy oil-light oil ratio of about 1:1 was obtained. No solid paraffin was observed in the reaction tube. The durability of the catalyst was increased considerably at the expense of a lower reaction rate; from the standpoint of durability, therefore, 12 percent is considered the most suitable uranium oxide content.

Cobalt-Copper Catalysts

According to experimental results obtained by Fischer, when nickel and cobalt are used as catalysts for the production of liquid hydrocarbons, an extended hydrogen reduction at high temperature is necessary - 3 hours at 450° C. for nickel[56] and 4 to 5 hours at 350° C. for cobalt.[57] Use of this strenuous reduction procedure on an industrial scale, however, is uneconomical, not only because of the cost of the hydrogen but also because the high reduction temperature necessitates frequent maintenance of the reduction equipment. Therefore, a catalyst requiring no hydrogen reduction or one that requires only a short reduction at a relatively low temperature would be highly desirable. A method of attacking this problem was suggested by the fact that the reduction temperature of oxides of iron, nickel, and cobalt can be lowered considerably by the addition of a small quantity of readily reducible metals, such as platinum, palladium, copper, or silver.

Cobalt-copper catalysts were first used in the hydrocarbon synthesis by Elvins,[58] Smith,[59] and Kodama[60] in early work on this problem. Copper, however, was first thought to be only a promoter, and the catalyst was normally used after hydrogen reduction at about 300° C. Fischer found later that the cobalt-copper catalyst did not require high-temperature hydrogen reduction and showed that reduction could be effected directly by synthesis gas at about 200°C.

56/ Work cited in footnote 12.
57/ Work cited in footnote 3.
58/ Work cited in footnote 22.
59/ Work cited in footnote 8.
60/ Work cited in footnote 9.

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Elvins[61] considered Co-Cu-Mn catalyst the best, and Smith[62] considered either Co-Cu-Mn or Co-Cu-U catalysts superior; Fischer[63] designated 9 Co:1 Cu:2 Th as his standard catalyst; Fujimura and Tsuneoka[64] obtained their highest yield of liquid hydrocarbons (145 ml./$m.^3$ of synthesis gas) by using 8 Co:1 Cu:0.2 Th:0.1 U catalyst. Cobalt-copper-catalysts have been prepared either by thermal decomposition of a mixture of the nitrate salts or by ignition with starches and cane sugar, as done by Fujimura;[65] such silica substances as diatomaceous earth and pumice have been used as carriers.

Preparation of catalysts according to the methods described above resulted in widely varying activities because of variations in preparation conditions, and a constant yield of liquid hydrocarbons could not be obtained. By precipitation with alkaline carbonate according to Fischer,[66] however, favorable results were obtained with nickel and cobalt catalysts.

Experimental Procedure

Catalyst preparation. - To a cobalt nitrate solution corresponding to 3 gm. of cobalt were added a copper nitrate solution containing a definite amount of copper and nitrate salt solutions containing definite amounts of manganese, thorium, calcium, barium, lead, cesium, aluminum, and chromium. Three grams of diatomaceous earth was then mixed in, and slightly more potassium carbonate than required for neutralization was added. The precipitate was filtered, desiccated at about 100° C., and charged to the reaction tube. When uranium oxide and tungsten oxide were used as promoters, they were obtained by dissolving ammonium uraniumate, obtained by adding uranium nitrate and ammonium to mixed carbonate salts of cobalt and copper and ammonium tungstate in concentrated nitric acid.

Results

Effects of reduction temperature. - Fischer[66] states that if 10 to 20 percent of copper is added to cobalt, the temperature of cobalt oxide is reduced from 350° C. to about 200° C. However, this is dependent on the type of catalyst used and the method of preparation. The resulting decreases in reduction temperature obtained by using 100 Co:10 Cu:12 U_3O_8 and 100 Co:10 Cu:15 Mn catalysts are shown in tables 18 and 19.

61/ Work cited in footnote 22.
62/ Work cited in footnote 8.
63/ Work cited in footnote 21.
64/ Work cited in footnote 4.
65/ Work cited in footnote 36.
66/ Work cited in footnote 21.

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TABLE 18. - Effect of the reduction temperature

(100 Co:10 Cu:12 U_3O_8:100 diatomaceous earth catalyst = 3 gm. Co; reaction temperature = 210° C.; gas velocity = 6 l./hr.; 72.0 l. of gas used in each case)

Experiment No.	Reduction temperature, °C.	Reduction time, hours	Gas contraction, percent	Liquid products, ml./m.^{3}	
				Gasoline (C_{5+})	Water
4A.....	200	1	74.0	138.0	180.5
4B.....	200	3	76.2	140.2	195.2
4C.....	250	1	75.8	138.5	190.2

TABLE 19. - Effect of the reduction temperature

(100 Co:10 Cu:15 Mn:100 diatomaceous earth catalyst = 3 gm. Co; gas velocity = 6 l./hr.)

Experiment No.	Reduction temperature, °C.	Reduction time, hours	Reaction temperature, °C.	Volume gas used, liters	Gas contraction, percent	Liquid products, ml./m.^{3}	
						Gasoline (C_{5+})	Water
48A.....	200	1	210	24.0	25.8	-	-
48B.....	200	1	220	24.0	30.0	-	-
48C.....	250	1	210	45.0	64.8	80.3	150.0
48D.....	250	3	210	45.0	70.2	108.5	168.5
48E.....	250	5	210	72.0	70.8	107.8	170.3

Virtually no change was found in the yield of gasoline (C_{5+}) when Co:Cu:U_3O_8 catalyst was reduced for 1 to 3 hours at 200° C. or for 1 hour at 250° C. In contrast to this, when Co:Cu:Mn catalyst was used, an unfavorable gas contraction was obtained with a hydrogen reduction of 1 hour at 200° or 250° C.; a desirable yield of gasoline was obtained only after hydrogen reduction for 3 to 5 hours at 250° C. To ascertain the reason for the different results produced by these low reduction temperatures, Co:Cu:U_3O_8:diatomaceous earth catalyst (100:10:12:100), which had been used in the synthesis for about 12 hours, was first air-oxidized at about 100° C. for an hour, followed by hydrogen reduction at 200° C. for an hour. When synthesis gas was then passed over the catalyst, the gas contraction was about 30 percent at 210° C., 35 percent at 220° C., and 50 percent at 230° C. Thereupon, hydrogen reduction was repeated at 250° C. for 1 hour, and a gas contraction of 68 percent was subsequently obtained at 210° C. It was not until the catalyst was reduced in hydrogen at 250° C. for 2 hours that the originial activity finally was obtained. Thus, the good results obtained in experiments 4A, B, and C, table 18, appear to be a result of the reducing action of the ammonia gas released by the dissolution of ammonium uraniumate during the preparation of the catalyst, and the reduction of cobalt oxide containing 10 percent copper for 1 hour at 200° or 250° C. is not adequate. Indications are that reduction for more than 3 hours at 250° C. is necessary.

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Fischer and Meyer[67] showed that ammonia gas lowered the temperature at which catalysts could be reduced, suggesting that, if a mixture of hydrogen and ammonia gas were used instead of hydrogen alone, about an hour's reduction at 200° C. would be enough. To verify this suggestion, a bottle filled with approximately a 10 percent aqueous ammonia solution was placed before the reaction tube, and the hydrogen was bubbled through it. By reducing the catalyst with this hydrogen-ammonia mixture for 1 hour at 200° C., activity comparable to that resulting from hydrogen reduction for 3 hours at 250° C. was obtained.

Effect of quantity of copper added. - The decrease in reduction temperature of cobalt oxide, based on the easily reducible property of copper, depends on the amount of copper (relative to the cobalt) contained in the catalyst. However, according to experimental results obtained by Armstrong and Hilditch,[68] Fischer,[69] and Kodama,[70] copper is not, itself, a catalyst for the synthesis of hydrocarbons from carbon monoxide-hydrogen mixtures. The function of copper, therefore, is merely to decrease the reduction temperature of cobalt oxide, or it may be thought of as acting as a type of promoter. (Fischer said that the production of cobalt carbide was accelerated by the reaction, $Co + Cu + CO = CoC + CuO$). Hence, the addition of more than the optimum amount of copper would, in a manner analogous to other promoters, cover the active centers of the cobalt and decrease the activity.

The optimum amount of copper, therefore, is that which will decrease the catalyst reduction temperature while maintaining a gasoline yield equal to or greater than that obtained when the catalyst is reduced for 4 to 5 hours at 350° C. (without the addition of copper). The gasoline yields obtained from Co-Cu-U_3O_8 catalysts (12 percent uranium oxide) containing various amounts of copper are shown in table 20.

From the gas contraction and the analyses of the synthesis and product gases shown in table 20, the rate of reaction between carbon monoxide and hydrogen and the percentages of carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons based on the carbon monoxide in the synthesis gas were obtained. The percentage of carbon monoxide converted to gasoline (C_{5+}) was obtained by adding these three values and subtracting their sum from 100, with the results shown in table 21.

67/ Fischer, F., and Meyer, K., [The Activating Action of Ammonia Upon the Reduction and Activity of Nickel Catalysts]: Brennstoff Chem., vol. 14, 1933, pp. 86-89.

68/ Armstrong, E. F., and Hilditch, T. P., Study of Catalytic Actions at Solid Surfaces X. The Interaction of Carbon Monoxide and Hydrogen as Conditioned by Nickel at Relatively Low Temperatures. A Practical Synthesis of Methane: Proc. Roy. Soc. (London), vol. 103A, 1923, pp. 25-34.

69/ Fischer, F., Tropsch, H., and Dilthey, P., [The Reduction of Carbon Monoxide to Methane in the Presence of Various Metals]: Brennstoff Chem., vol. 6, 1925, pp. 265-271.

70/ Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure I. Studies of the Catalytic Activity of a Few Metals by the Heating Curve Method]: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 7; Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 277-283; abstracts section (in German), vol. 2, 1929, pp. 35-36.

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TABLE 20. - Effect of copper concentration

(100 Co:12 U_3O_8:100 diatomaceous earth + Cu catalyst = 3 gm. Co; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used except as noted.)

Experiment No.	Cu content, percent of Co in catalyst	Composition of synthesis gas			Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m.^{3}		Product gas composition, percent						
		CO	H_2	N_2			Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
49a/	0	32.0	64.8	3.2	200	77.5	134.5	181.6	2.0	-	24.0	46.8	12.6	1.20	14.6
50A	20	33.2	63.4	3.4	200	62.5	107.5	158.2	1.8	-	31.2	53.0	3.4	2.42	10.6
50B	20	33.0	64.5	2.5	210	74.5	137.5	185.6	2.6	0.2	28.4	52.5	7.4	1.80	8.9
3	10	32.6	64.0	3.4	200	60.4	110.6	150.5	2.6	-	30.0	56.1	2.4	2.97	8.9
4	10	32.5	65.2	2.3	210	74.0	138.0	180.5	4.6	0.2	24.4	54.2	7.7	1.85	8.9
18A	5	32.5	64.8	2.7	190	75.4	133.3	179.2	2.0	-	20.0	57.7	10.3	1.53	10.0
18B	5	32.8	65.0	2.2	200	80.6	143.3	193.5	4.6	0.2	23.4	43.8	16.5	1.31	11.5
51A	2.5	32.8	64.4	2.8	190	78.4	137.5	178.5	2.6	.2	29.4	47.0	8.4	1.62	12.4
51B	2.5	33.0	64.4	2.6	200	81.2	143.5	191.7	3.8	.4	30.7	39.0	13.7	1.30	12.4

a/ 154 l. of synthesis gas used.

TABLE 21. - Effect of copper concentration

Experiment No.	CO conversion, percent	H_2 conversion, percent	Carbon distribution, percent of CO in synthesis gas			
			CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})
49	82.6	84.8	1.5	17.4	11.0	70.1
50A	64.8	68.7	2.0	35.2	9.3	53.5
50B	78:1	79.2	2.0	21.9	10.3	65.7
3	63.6	65.6	3.2	36.4	8.7	51.7
4	80.5	78.4	3.7	19.5	10.6	66.2
18A	84.9	78.1	1.5	15.1	11.9	71.5
18B	86.2	86.9	2.7	13.8	12.8	70.7
51A	80.6	84.2	1.7	19.4	8.9	70.0
51B	82.5	88.6	2.2	17.5	10.1	70.2

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Experiment 49. - In accordance with the experimental results obtained by Fischer and Koch, hydrogen reduction for 4 to 5 hours at 350° C. resulted in a production of 137.5 ml. of gasoline per cubic meter of synthesis gas at 200° C. As the catalyst life increased (volume of gas used increased from 72.0 to 154.0 liters), the yield of gasoline decreased slightly to 132.0 ml./m^3.

Experiments 50A and B. - This catalyst, containing 20 percent copper, was reduced for about 1 hour at 200° C., after which synthesis gas was introduced at the same temperature, with the production of 107.5 ml. of gasoline per cubic meter of synthesis gas. When the reaction temperature was raised to 210° C., this yield was increased to 137.5 ml./m^3, essentially that obtained when the catalyst was reduced at 350° C. without the addition of copper.

Experiments 3, 4, and 18A and B. - The copper content was decreased to 10 percent and 5 percent in these experiments, and the catalysts were reduced at about 200° C. for an hour, after which synthesis gas was introduced. The yield of gasoline increased with decreasing copper content; a maximum of 143.3 ml./m^3 of synthesis gas was obtained at 200° C., when the copper content was 5 percent of the cobalt. This yield of gasoline is slightly more than that obtained in experiment 49, in which no copper was added.

Experiments 51A and B. - The copper content of the catalyst was decreased still further to 2.5 percent. After hydrogen reduction for about an hour at 200° C., synthesis gas was introduced. These conditions produced gasoline yields of 0 percent at 200°, 12 percent at 210°, and 80 percent at 220° C. After an hour's operation at 220°, the reaction temperature was lowered to 210° C., and the yield of gasoline remained at 80 percent. This demonstrates that reduction of cobalt oxide in hydrogen for 1 hour at 200° C. is completely ineffective when 2.5 percent of copper has been added. Accordingly, the catalyst was reduced in hydrogen at 250° C. for 1 hour in order to complete the reduction; gasoline yields of 137.5 and 145.8 ml./m^3 of synthesis gas were obtained at 190° and 200° C., respectively.

From these results, it appears that (1) the yield of gasoline (based on carbon monoxide in the synthesis gas) tends to increase with decrease in the content of copper relative to cobalt; (2) if mild reduction conditions are used, and if synthesis is to be started immediately after the reduction treatment, a copper content of more than 5 percent is necessary; and (3) a catalyst containing copper and which has been reduced for a short time at about 200° C. has a higher activity than a catalyst that has been reduced for a long time at 350°C. These points substantiate the theory that copper not only decreases the reduction temperature of cobalt oxide but also functions as a promoter for cobalt. It is still doubtful whether, as Fischer has stated, copper functions as a promoter in the production of cobalt carbide by the reaction $Co + Cu + CO = CuO + CoC$.

Effect of promoters. - The effects of promoters were observed by adding 15 percent each of the following compounds (based on cobalt) to 100 Co:5 Cu catalyst: CaO, BaO, WO_3, U_3O_8, CeO_2, PbO, ZnO, ThO_2, CdO, MnO, Al_2O_3, Cr_2O_3, and MgO. The results found for U_3O_8, CeO_2, ThO_2, and MnO are shown in table 22; only these compounds exhibited any promoting effect.

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TABLE 22. - The effect of promoters

(100 Co:5 Cu:15 promoter:100 diatomaceous earth catalyst = 3 gm. Co; gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Promoter	Reaction temperature, °C.	Gas contraction, percent	Liquid products, ml./m.^{3}	
				Gasoline (C_{5+})	Water
52.....	CeO_2	210	41.4	38.6	98.1
53.....	U_3O_8	200	80.8	150.5	212.0
54.....	ThO_2	210	75.2	122.5	185.6
48D.....	MnO	210	70.2	108.5	168.5

Experiment 52. - Cerium oxide was first used as a promoter for cobalt-copper catalysts by Erdley and Nash,[71] who observed that although the activity was large in the first stages of the reaction it decreased with time at an increasing rate. Kodama[72] stated that cerium oxide was inferior to zirconia and magnesium oxide as a promoter for cobalt-copper catalysts. Experiment 52, using a catalyst in which cerium oxide was precipitated together with cobalt and copper as mixed carbonate salts, had a low activity and produced only 30.6 ml. of gasoline (C_{5+}) per cubic meter of synthesis gas at 210° C.

Experiment 53. - Uranium oxide was used as a promoter for cobalt-copper catalysts by Smith, et al, and by Fujimura, et al. The author also found it to be very effective by adding it to nickel carbonate catalyst. In experiment 53, cobalt and copper were precipitated as mixed carbonate salts by potassium carbonate, and uranium oxide was precipitated as ammonium uraniumate by ammonia. The catalyst thus prepared was very active. After hydrogen reduction for 1 hour at 200° C., 150.5 ml. of gasoline was obtained per cubic meter of synthesis gas at a reaction temperature of 200° C.; small quantities of solid paraffin were deposited at the end of the reaction tube in the final stages of the synthesis.

Experiment 54. - Co-Cu-ThO_2 catalysts were prepared by calcination by Kodama and Fischer and by precipitation by Watanabe. After 3 hours of hydrogen reduction at 250° C., a gas contraction of 75.2 percent was obtained at a reaction temperature of 210° and 122.5 ml. of gasoline was produced per cubic meter of synthesis gas. Although these results are inferior to those obtained with uranium, no solid paraffin was formed when thoria was used. The preparation of thoria-promoted catalysts require special precautions, however, as basic thorium carbonate may dissolve in excess potassium carbonate.

Experiment 48D. - Co-Cu-Mn catalysts were first studied by Smith and then by Fischer, who used a catalyst precipitated by sodium carbonate; a maximum gasoline yield of 118 ml./m.^{3} of synthesis gas was obtained. The use of manganese as a promoter in experiment 48D, however, produced a gasoline yield of only 108.5 ml./m.^{3} of synthesis gas after a hydrogen reduction at 250° C. for 3 hours, thus failing to reproduce the results obtained by Fischer et al.

The above results show that uranium oxide is the most satisfactory promoter and that thoria, manganese oxide, and cerium oxide are decreasingly effective in that order. Further studies of Co-Cu-U_3O_8 catalyst were made on samples -

71/ Work cited in footnote 7.
72/ Work cited in footnote 51.

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containing 12 percent, 6 percent, and 3 percent uranium oxide, respectively, in an attempt to decrease the formation of solid paraffin as the formation of such material lowers the durability of the catalyst. The results are shown in table 23.

Experiments 55 and 56. - Decreasing the uranium oxide content from 15 percent to 12 percent, 6 percent, and 3 percent reduced the gasoline yield (after reduction for 1 hour at 200° C.) from 150.5 to 143.3, 137.5 and 95.6 ml./$m.^3$ of synthesis gas, respectively, at a reaction temperature of 200° C.

Consideration of the ratio between the relatively heavy oil condensed in the burette and the light oil absorbed by the activated carbon shows that production of light oil is favored by decreased quantities of uranium oxide, and that production of gaseous hydrocarbons is increased simultaneously. Thus, table 24 shows a heavy oil:light oil ratio of 2.3:1, 2.1:1, and 1.0:1 at uranium oxide contents of 15, 12, and 6 percent, respectively; the values listed in this table were calculated from the data given in table 23.

From table 24, it is evident that the conversion of carbon monoxide is about the same in all three cases. Hence, changes in the gasoline yield may be considered as dependent chiefly on the quantity of gaseous hydrocarbons produced. Although an increase in the production of gasoline would be desirable, any attempt to do this by increasing the heavy-oil production results in formation of an increasing quantity of solid paraffins.

The addition of manganese to Co-Cu-U_3O_8 catalysts produced the results shown in table 25.

The percentages of carbon dioxide, carbon monoxide, gaseous saturated hydrocarbons, and gasoline in the product gases, based on the carbon monoxide in the synthesis gas, were calculated by the usual method and are shown in table 26.

Experiments 58, 59, and 60. - Addition of 16 and 8 percent manganese to 100 Co:5 Cu:12 U_3O_8 catalyst accelerated the production of gaseous hydrocarbons and decreased the yield of gasoline. A manganese content of 4 percent, however, showed a promoting effect, increasing the gasoline yield from 143.3 to 158.2 ml./$m.^3$ of synthesis gas.

Experiment 61. - Decreasing the uranium oxide content to 6 percent produced essentially the same results obtained with a uranium oxide content of 12 percent. About 4 percent manganese was found to be most suitable, a large manganese content having an accelerating effect upon the production of gaseous hydrocarbons.

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TABLE 23. - Effect of promoters

(100 Co:5 Cu:100 diatomaceous earth + U_3O_8 catalyst = 3 gm. Co; reaction temperature = 200° C.; gas velocity = 6 l./hr.; 72.0 l. synthesis gas used in each case)

Experiment No.	U_3O_8, percent of Co in catalyst	Composition of synthesis gases, percent			Gas contraction, percent	Liquid products, ml./m.3		Product gas composition, percent						
		CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_mH_{2n+2}	n	N_2
55.....	12	32.8	64.4	2.8	80.6	143.3	193.5	4.6	0.2	23.4	43.8	16.5	1.38	11.5
56.....	6	33.0	64.0	3.0	82.5	137.5	200.0	5.0	.4	20.8	31.9	26.8	1.20	15.1
57.....	3	33.0	63.8	3.2	62.4	95.6	166.5	1.0	.2	30.5	54.8	5.4	1.40	8.1

TABLE 24. - Effect of promoters

Experiment No.	CO conversion, percent	Carbon distribution, percent of CO in synthesis gas			
		CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})
53.....	85.2	2.2	14.8	10.9	72.1
55.....	86.2	2.7	13.8	12.8	70.7
56.....	89.0	2.7	11.0	17.1	69.2
57.....	65.2	1.1	34.8	8.6	55.5

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TABLE 25. - Effect of promoters

(Gas velocity = 6 l./hr.; 72.0 l. of synthesis gas used in each case)

Experiment No.	Catalyst composition				Reaction temperature, °C.	Synthesis gas composition, percent			Gas contraction, percent	Liquid products, ml./m.^{3}		Product gas composition, percent						
	Co	Cu	U_3O_8	Mn		CO	H_2	N_2		Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
58.....	100	5	12	16	200	32.0	65.3	2.7	70.4	120.8	180.0	4.6	-	22.0	50.8	11.3	1.14	11.3
59.....	100	5	12	8	200	32.0	65.0	3.0	75.5	125.0	183.3	2.0	0.4	20.4	44.8	20.4	1.12	12.0
60.....	100	5	12	4	195	32.2	65.0	2.8	82.4	158.2	205.5	2.8	.2	20.0	50.5	12.4	1.88	14.1
61.....	100	5	6	4	195	31.8	65.4	2.8	78.8	150.0	210.5	1.8	.2	20.8	48.5	15.4	1.26	13.3

TABLE 26. - Effect of promoters

Experiment No.	Co conversion, percent	Carbon distribution, percent of CO in synthesis gas			
		CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})
58.....	79.6	4.2	20.4	11.9	64.5
59.....	84.4	1.5	15.6	17.3	65.6
60.....	89.1	1.5	10.9	12.7	74.9
61.....	86.1	1.2	13.9	12.9	72.0

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Cobalt-Nickel-Copper Catalysts

As the temperature of cobalt oxide was successfully reduced from 350° to 250° C. by the addition of more than 5 percent of copper, a similar application in the case of nickel catalysts was proposed. According to Fischer and Meyer[73] and Fujimura and Tsuneoka,[74] copper is ineffective in lowering the reduction temperature of nickel; unless hydrogen reduction is carried out at 450° C., no liquid hydrocarbons are produced, and, even after such reduction, the yield is small. According to Fischer and Meyer,[75] when a Ni-Mn-Al_2O_3 catalyst containing only 0.1 percent copper (based on nickel) was reduced at 450° C., the yield of liquid hydrocarbons decreased rapidly from 120 to 84 ml./$m.^3$ of synthesis gas. According to Fujimura and Tsuneoka,[76] there is no increase in the yield of liquid hydrocarbons obtained from Ni-Mn catalyst containing up to 9.5 percent copper. At copper contents above 1 percent, the catalytic activity of nickel catalyst is impaired, whereas copper contents below 0.5 percent are ineffective in decreasing the reduction temperature of nickel. This difference in behaviour between cobalt and nickel catalysts was explained by Fischer[77] on the following basis. He postulated that copper has only an extremely weak tendency to form alloys with cobalt at synthesis temperatures; in cobalt catalysts, therefore, copper can function as a promoter. The ineffectiveness of copper as a promoter for nickel catalysts may be explained by one of the following mechanisms: (1) Either the reduction temperature of nickel oxide is lowered by the addition of copper, followed by combination of the reduced nickel with copper in any proportion to form mixed crystals, thereby destroying any catalytic properties suitable for this reaction, or (2) the reduction temperature of nickel is not lowered by the addition of copper, and, after reduction at high temperature, the nickel forms mixed crystals with copper with results comparable to (1).

From the observation that hydrogen reduction at 450° C. was necessary both when copper had been added and when copper had not been added to nickel catalysts, the author considered case (2) to be most probable. As the addition of cobalt to nickel catalysts did not impair their activities, an attempt was made to lower the reduction temperature of nickel catalysts by the addition of cobalt, the reduction temperature of which had been lowered by copper.

Results

The experimental results obtained by varying the proportion of cobalt to nickel and the proportion of copper with respect to the sum of cobalt and nickel in a Co-Ni-Cu-U_3O_8 catalyst are shown in table 27.

73/ Fischer, F., and Meyer, K., [The Reducibility of Standard Nickel Catalyst]: Brennstoff Chem., vol. 14, 1933, pp. 64-67.
74/ Work cited in footnote 48.
75/ Work cited in footnote 73.
76/ Work cited in footnote 48.
77/ Work cited in footnote 21.

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TABLE 27. - Cobalt-nickel-copper catalysts

(Catalyst equivalent to 3 gm. of Co; gas velocity = 6 l./hr.)

Experiment No.	Catalyst composition				Reaction temperature, °C.	Volume gas used, l./hr.	Gas contraction, percent	Liquid products, ml./m.^{3}	
	Co	Ni	Cu	U_3O_8				Gasoline (C_{5+})	Water
62.....	50	50	0	12	190	72.0	84.5	145.6	205.2
63.....	80	20	10	12	200	72.0	80.2	140.5	200.0
64A.....	50	50	5	12	210	54.0	67.8	91.7	141.7
64B.....	50	50	5	12	220	54.0	70.2	116.6	175.0
65A.....	50	50	10	12	205	72.0	78.4	137.5	205.0
65B.....	50	50	10	12	215	72.0	76.8	120.8	198.2
66.....	20	80	10	12	215	36.0	58.2	66.6	106.6
67.....	20	80	20	12	220	36.0	55.6	60.0	98.8
68.....	10	90	10	12	220	36.0	-	-	-
69.....	10	90	20	12	220	36.0	-	-	-
70.....		80	20	12	220	36.0	-	-	-
71.....		50	50	12	220	36.0	-	-	-

Experiment 62. - Half the amount of cobalt in the catalyst used in experiment 49 was replaced by nickel. Following hydrogen reduction at 400° C. for 4 hours, synthesis gas was introduced at 190° C.; 145.6 ml. of gasoline (C_{5+}) and 205.2 ml. of water was produced per cubic meter of synthesis gas. These results do not differ greatly from those of experiment 49, and it is apparent that the catalytic nature of the cobalt was in no way impaired by the addition of nickel.

Experiment 63. - In this catalyst, 20 percent of the cobalt was replaced by nickel, and 10 percent copper (relative to Ni + Co) was added. After hydrogen reduction at 200° C. for 1 hour, synthesis gas was introduced, and 140.5 ml. of gasoline and 200.0 ml. of water were produced per cubic meter of synthesis gas. No significant difference between these results and those of experiment 52 (when nickel was not added) is evident. The reduction temperature of this cobalt catalyst was in no way affected by the substitution of 20 percent nickel.

Experiment 64A and B. - A catalyst containing a nickel:cobalt ratio of 1:1 and 5 percent copper was reduced in hydrogen for 1 hour at 200° C. Operation in the synthesis produced a gas contraction of 0 percent at 200° C., 12 percent at 210° C., and 60 percent at 220° C. After an hour at 220° C., the temperature was lowered to 210°, and the gas contraction remained at about 60 percent, clearly showing that a reduction temperature of 200° C. was inadequate. Hydrogen reduction was then carried out for 3 hours at 250° C., after which 91.7 ml. of gasoline and 141.7 ml. of water were produced at 210° C. per cubic meter of synthesis gas. Comparison with experiments 18A and B indicated that the activity of this catalyst was reduced considerably, suggesting that, at a copper content of 5 percent, the reduction of 1Ni:1Co catalyst was quite inadequate even after 3 hours at 250° C.

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Experiment 65A and B. - The copper content of 1Ni:1Co catalyst was increased from 5 percent to 10 percent. Synthesis gas was introduced after 1 hour's reduction at 200° C., producing a gas contraction of 60 percent at 200° and 80 percent at 210°, indicating that these conditions were nearly sufficient for complete reduction of this catalyst. After reduction for 1 hour at 250° C., 137.5 ml. of gasoline was produced per cubic meter of synthesis gas at a reaction temperature of 205° C., a value that decreased to 120.8 ml./$m.^3$ at a reaction temperature of 215° C. These results are very similar to those of experiment 47, in which the catalyst contained no cobalt or copper, and experiments 3 and 4, in which the catalyst contained no nickel. Thus, depending on the starting material, either half of the cobalt may be replaced by nickel in 100 Co:10 Cu:12 U_3O_8 catalyst, or half the nickel may be replaced by cobalt and 10 percent copper added to 100 Ni:12 U_3O_8 catalyst without any subsequent loss in catalyst activity, and, in the latter case, the necessary reduction temperature is decreased from 450° to 200° to 250° C.

Experiment 66. - Increasing the Ni:Co ratio to 8:2 in the presence of 10 percent copper and utilizing a reduction at 200° C. for 1 hour produced a gas contraction of 10 percent at 210° C. and 30 percent at 220° C. Reduction of the catalyst for 3 hours at 250° C. resulted in a gasoline yield of 66.6 ml. and a yield of water of 106.6 ml. per cubic meter of synthesis gas at a reaction temperature of 220° C. More complete reduction of the catalyst was thus indicated.

Experiment 67. - In this catalyst, the copper content was increased from 10 percent to 20 percent. However, after hydrogen reduction at 200° C., the resulting gas contraction was not large, and after hydrogen reduction for 3 hours at 250° C., only 60.0 ml. of gasoline and 98.8 ml. of water were produced per cubic meter of synthesis gas at 220° C.; therefore, a decrease in the activity of this catalyst from that exhibited by a catalyst containing 10 percent copper is evident. These results suggest that increasing the copper content from 10 percent to 20 percent decreases the reduction temperature of this catalyst still further, but that copper itself possesses no promoting characteristics as applied in this reaction. As in the general case of promoters, the addition of copper in excess of the optimum amount covers the active centers of the catalyst and gradually reduces its activity. A decrease in the reduction temperature of 8 Ni:2 Co catalyst by the addition of copper is accompanied by a loss in catalytic activity.

Experiments 68 and 69. - Increasing the Ni:Co ratio to 9:1 and the copper content to 20 percent produced no appreciable catalyst activity at reaction temperatures as high as 225° C. after reduction in hydrogen for 3 to 4 hours at 250° C.

Experiments 70 and 71. - These catalysts contained no cobalt, and copper contents of 10, 20, and 50 percent (based on the nickel) were tried. After reduction for 4 hours at 250° C., no activity could be detected at reaction temperatures as high as 230° C.

The above results show that the activity of Ni-Cu-U_3O_8 catalyst is not enhanced by the addition of cobalt, and that decreasing the reduction temperature of nickel oxide from 450° to 200° to 250° C. without simultaneously decreasing the activity requires the addition of an amount of cobalt equivalent to or greater than that of the nickel.

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Recently, Tanaka and Kobayashi[78] concluded that the reduction temperature of nickel-copper catalysts is lower than that of either nickel or copper alone. According to Armstrong,[79] in the reduction of nickel-copper catalysts, copper oxide is first reduced; as this is an exothermic reaction, reduction of the nickel oxide is favored by the resulting heat of reaction. However, the activity of copper-containing catalysts depends largely upon the reduction conditions. For example, reduction of copper oxide in a rapid stream of hydrogen produces a white heat as a result of the exothermic nature of the reaction; the copper thus formed is very red, and its catalytic activity is extremely low. Conversely, reduction in a slow stream of hydrogen produces copper having a faint violet color and possessing a vigorous catalytic activity. On this basis, the reduction of Co-Cu-U_3O_8 and Ni-Cu-U_3O_8 catalysts may be considered to proceed first by the reduction of copper oxide; the reduction of the oxides of nickel and cobalt are then accelerated by the heat of reaction liberated at this time. The tendency to form mixed crystals of cobalt and copper is weak, but nickel and copper easily form mixed crystals, especially at local hot spots caused by the heat of reaction. Thus, the surface of the resulting catalyst is in a semi-sintered state, and its catalytic activity is extremely low. The reduction of cobalt oxide and nickel oxide in the absence of copper proceeds at 350° and 450° C., respectively. Therefore, a greater amount of energy must be released to accelerate the reduction of nickel oxide than is required to similarly affect cobalt oxide. Indeed, Co-Cu-Th catalysts prepared by the calcination method become virtually inactive when reduced in hydrogen at 350° C.[80] Experimental results show that although the reduction of copper oxide accelerates the reduction of the nickel oxide component, insufficient energy is released by the copper oxide reaction to completely accomplish this objective. Is this conclusion compatible with the fact that the reduction temperature of nickel oxide was successfully lowered by the action of a large amount of cobalt and copper? Yes, because an additional source of heat is available from the conversion of cobalt oxide to cobalt. Copper oxide was first reduced, and its heat of reaction accelerated the reduction of cobalt oxide, with the result that more heat energy was released to accelerate the reduction of nickel oxide. A larger amount of cobalt oxide is needed to sustain its own reduction and that of nickel oxide as the proportion of copper oxide is decreased.

If, as the above discussion indicates, the reduction of nickel oxide-copper catalyst is incomplete at 250° C., the question is pertinent as to exactly what percent reduction is necessary for nickel, cobalt, and iron catalysts to make them good catalysts for the synthesis of liquid hydrocarbons from hydrogen and carbon monoxide. According to Antheaume,[81] iron catalysts

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78/ Tanaka, Y., and Kobayashi, R., [High-Pressure Hydrogenation of Fatty Oils III. Production of Active Catalysts by Reduction of Mixed Hydroxides of Nickel and Copper in Liquid Medium]: Jour. Soc. Chem. Ind. Japan, vol. 36, 1933, p. 24; supplemental binding pp. 36-37.

79/ Armstrong, E. F., and Hilditch, T. P., Study of Catalytic Actions at Solid Surfaces IX. The Action of Copper in Promoting the Activity of Nickel Catalyst: Proc. Roy. Soc. (London), vol. 102A, 1922, pp. 27-32.

80/ Work cited in footnote 3.

81/ Antheaume, J., Decarriere, E., and Reaut, R., [Physicochemical Study of Iron Catalyst Used in the Synthesis of Liquid Hydrocarbons]: Chim. et Ind. Special No., vol. 31, 1934, pp. 421-423.

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function in this catalytic capacity as Fe_3O_4. However, nickel and cobalt catalysts react in a manner entirely different from that of iron catalysts; as their capacity for hydrogenation is high, they should be used in the form of mixtures of reduced metal and oxides. The hydrogenating ability of nickel catalysts is much superior to that of cobalt catalysts, and, when used for this purpose, nickel catalysts may be reduced, in the absence of diatomaceous earth, at about 300° C., whereas, for cobalt catalysts a temperature of more than 400° C. is required. In the hydrocarbon synthesis, however, reduction of cobalt is carried out at 350° C., whereas nickel requires a temperature of 450° C. Furthermore, whereas cobalt-copper catalysts can, without preliminary hydrogen reduction, initiate reaction with synthesis gas immediately, nickel-copper catalysts require previous hydrogen reduction at high temperatures. These observations suggest that the extent of reduction of nickel catalysts must be greater than that of cobalt catalysts for this reaction; in other words, the quantity of reduced metal relative to metal oxides in the nickel catalysts must be comparatively greater than in the case of cobalt catalysts.

Catalysts Containing Silver

It is well known that silver oxide can easily be used to separate metals by the application of heat at relatively low temperatures. This suggests that, like copper, silver can be added to cobalt oxide or to nickel oxide catalysts to lower their reduction temperatures. Accordingly, silver was added to cobalt oxide and nickel, and its effects upon them were observed. In preparing these catalysts, silver nitrate was used as a source of silver; nickel and cobalt carbonates were precipitated by potassium carbonate, and uranium oxide was used as a promoter.

Results

The results of these experiments are shown in tables 28 and 29.

Experiment 72. - This catalyst contained 10 percent of silver based on the cobalt. After hydrogen reduction for an hour at 200° C., synthesis gas was introduced; gas contractions of 0 percent at 200°, 20 percent at 210°, and 60 percent at 230° C. were found. These poor results were attributed to inadequate reduction, so the catalyst was reduced for 2 hours at 250° C. As a result, at 180° C. 154.2 ml. of gasoline (C_{5+}) was produced per cubic meter of synthesis gas. Comparison of these results with those of experiments 3 and 4, in which 10 percent of copper was added, shows that silver is inferior to copper in lowering the reduction temperature of cobalt oxide, as the copper-containing catalyst was reduced successfully at 200° C; on the other hand, whereas the reaction temperature of the copper-containing catalyst was 210° C., the silver-containing catalyst exhibited an adequate activity at the relatively low temperature of 180° C., whereas the yield of gasoline was increased considerably. Thus, silver is superior to copper as promoter.

Experiment 73. - In this catalyst, the silver content was increased to 20 percent, resulting in a satisfactory activity after hydrogen reduction for an hour at 200° C. At a reaction temperature of 180° C., 148.2 ml. of gasoline was produced per cubic meter of synthesis gas, a result not materially different from that obtained with the catalyst containing 10 percent silver.

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TABLE 28. - Catalysts containing silver

(Weight of catalyst used equivalent to 3 gm. of Co or Ni; gas velocity = 6 l./hr.)

Experiment No.	Catalyst composition				Reaction temperature, °C.	Volume gas used, l.	Contraction, percent	Synthesis gas composition, percent			Liquid products, ml./m.^{3}		Product gas composition, percent						
	Co	Ni	Ag	U_3O_8				CO	H_2	N_2	Gasoline (C_{5+})	Water	CO_2	C_mH_n	CO	H_2	C_nH_{2n+2}	n	N_2
72....	100		1	12	180	72.0	84.2	31.8	65.2	3.0	154.2	205.4	3.4	-	16.2	46.9	16.2	1.95	17.3
73....	100		2	12	180	72.0	83.0	-	-	-	148.6	200.2	-	-	-	-	-	-	-
74....		100	1	12	210	54.0	58.0	32.0	64.8	3.2	28.6	-	17.4	-	.8	30.6	41.9	1.11	9.3
75....			2	12	220	54.0	34.0	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 29. - Catalysts containing silver

Experiment No.	CO conversion, percent	H_2 conversion, percent	Carbon distribution, percent of CO in synthesis gas			
			CO_2	CO	C_nH_{2n+2} (C_1-C_4)	Gasoline (C_{5+})
72.....	92.0	88.6	1.7	8.0	14.7	75.6
74.....	98.9	78.3	22.8	1.1	61.0	15.1

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Experiment 74. - This catalyst contained 10 percent silver based on the nickel. Hydrogen reduction was carried out for 3 hours at 250° C., and a gas contraction of 38 percent was obtained at a reaction temperature of 210° C. After more strenuous reduction for 1 hour at 300° C., this catalyst yielded a gas contraction of only 58 percent with a gasoline yield of only 28.6 ml./$m.^3$ of synthesis gas, and it is evident from the composition of the product gases that the greater part of the carbon monoxide was converted to carbon dioxide and gaseous saturated hydrocarbons. From previous observations, a decrease in the reaction temperature may be expected to increase the amount of gasoline produced. When the temperature was lowered to 200° and 190° C., the gas contraction decreased rapidly to 42 and 26 percent, respectively; and when 36.0 liters of synthesis gas was used, the respective gasoline yields were 38.2 ml. at 200° and 20.5 ml. at 190° C. per cubic meter of synthesis gas. Considering that similar catalysts containing 10 percent copper showed no activity at reaction temperatures up to 230° C., silver is superior to copper as an agent for lowering the reduction temperature of nickel oxide.

Experiment 75. - The silver content of the catalyst was increased to 20 percent, and hydrogen reduction was carried out for 1 hour at 300° C. The results are poorer than those for catalysts containing 10 percent silver; the gas contraction was only 34 percent at 220° C., and only a trace of gasoline was produced.

MECHANISM OF THE HYDROCARBON SYNTHESIS

Although no definite experimental evidence exists to support any postulated reaction mechanism for the synthesis of olefin and paraffin hydrocarbons from carbon monoxide and hydrogen, Fischer's carbide theory is considered the most probable. According to this theory, carbon monoxide first combines with either the nickel or the cobalt in the catalyst to form nickel or cobalt carbide. This carbide reacts with hydrogen to form free radicals, such as CH-, CH_2, and CH_3, which polymerize and take on hydrogen to form various olefin and paraffin hydrocarbons. The formation of carbide and carbon dioxide from nickel, cobalt, or their oxides and carbon monoxide has been established. Thus, the reaction between nickel and carbon monoxide is represented by:

$$3Ni + 2CO = Ni_3C + CO_2.$$

Although Fischer's mechanism postulates that free radicals polymerize and that the production of liquid hydrocarbons is accompanied by a large production of carbon dioxide without the formation of water, direct experimental results show that approximately 1-1/2 times more water than oil is produced, and no more than 2 or 3 percent of carbon dioxide is obtained under normal circumstances.

To explain this, Fischer stated that in the synthesis of liquid hydrocarbons the union of carbon and oxygen in carbon monoxide was first severed in the presence of nickel or cobalt catalyst, at which time the carbon combined with the activated metal to form carbides, and the oxygen reacted immediately with activated hydrogen to form water. However, various investigators, who passed carbon monoxide over nickel or cobalt with the formation of carbide, then passed hydrogen over the carbide and obtained the carbon of the carbide principally as gaseous hydrocarbons (chiefly methane); no liquid hydrocarbons were observed.

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Any explanation for catalytic activity is generally based on the presumption that the reaction takes place via an intermediate compound formed between the catalyst and the reactants. However, considering that the amount of active catalyst existing at any one time is extremely small (for instance, in the reaction, $C_6H_5NO_2 + 6H_2 = C_6H_{11}NH_2 + 2H_2O$, when reduced nickel is used, the probable amount of active nickel engaged in the reduction is 0.385 percent;[82] whereas, when ammoniated iron-alumina catalyst is used, the amount of active iron element is 0.25 percent[83]), it is evident that the formation of carbides at these active centers and their reaction with hydrogen would result in the formation of quantities of liquid hydrocarbons so small that they could hardly be detected. Furthermore, comparison of the case where carbon monoxide and hydrogen co-exist with the case where carbon monoxide does not exist, but where only hydrogen and carbide co-exist, shows a great difference between the equilibrium relationships in the two cases. The validity of either theory cannot immediately be judged, therefore, on the basis of the experimental results previously described.

Formation of Carbides

Much research has been carried out on the reaction of carbon monoxide with nickel, cobalt, iron, and their oxides. Bahr and Bahr[84] maintained that at temperatures below 270° C. nickel and carbon monoxide react quantitatively to form Ni_3C and that at increased temperatures Ni_3C (in this case metallic nickel does not exist at all) reacts still further with carbon monoxide to form Ni_xC and carbon dioxide. At temperatures above 380° to 420° C., Ni_3C decomposes into nickel and carbon, and this nickel is postulated as accelerating the decomposition of carbon monoxide.

In this respect, Horiba and Ri[85] made the following claims:

1. Ni_3C is formed only at the active centers of the catalyst.

2. Because of the formation of Ni_3C, catalysis of the decomposition of carbon monoxide is reduced.

3. Carbon monoxide reactions take place only on the remaining active centers of the nickel surface.

According to Tutiya,[86] at temperatures below 285° C., nickel and nickel oxide react with carbon monoxide to form Ni_3C and Ni_xC. Nickel on the surface

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82/ Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 31, 1925, p. 223. (Reference could not be located.)

83/ Almquist, J. A., The Nature of the Catalyst Surface and the Effect of Promoters: Jour. Am. Chem. Soc., vol. 48, 1926, pp. 2820-2826.

84/ Bahr, H. A., and Bahr, Th., [Decomposition of Carbon Monoxide on Nickel]: Ber., vol. 61B, 1928, pp. 2177-2183; [Reactions of Nickel Carbide (Ni_3C) Prepared at Low Temperatures]: Ber., vol. 63B, 1930, pp. 99-102.

85/ Horiba, S., and Ri, T., [Taylor's Theory of Active Centers and the Kinetics of Heterogeneous Gaseous Reactions]: Rec. trav. chim., vol. 51, 1932, pp. 641-647.

86/ Tutiya, H., [Catalytic Decomposition of Carbon Monoxide IV. Behaviour of Nickel Carbides]: Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 951-973.

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of the Ni_3C adsorbs the carbon monoxide; at temperatures of 265° to 275° C., carbon monoxide is adsorbed only in the presence of Ni_3C. Tutiya stated that in this case the process $Ni \xrightarrow{CO} Ni_3C \xrightarrow{CO} Ni_xC \longrightarrow Ni_3C + C$ existed. Ni_xC (nickel supercarbides) are extemely unstable, decomposing rapidly at about 280° C., and the pyrophoric nature of nickel carbide is really a result of this reaction.

Fischer, in his experiment,87/ reacted cobalt with carbon monoxide to form Co_3C_2 and obtained hydrocarbons from the carbide corresponding only to Co_3C. Tutiya88/ found Fe_3O_4 and Fe_3C (also carbides of other indefinite forms) when reacting iron oxide and carbon monoxide at 320° C. but did not find Fe_3O_4 or Fe_xC (supercarbides) at 270° C. In other words, Tutiya postulated that at temperatures above 280° C. such processes as $Fe_2O_3 \xrightarrow{CO} Fe_3C \xrightarrow{CO} Fe_xC \longrightarrow Fe_3C + C$ exist.

From the above experimental evidence, there is no doubt that carbon monoxide reacts with nickel, cobalt, or iron to form carbides of special composition. The speed of formation of such carbides is greatly influenced by the condition of the metal surface and by the method of its preparation. That is, the greater the activity of the catalyst, the lower the temperature and the greater the rate at which carbide is formed. The observation has previously been made that when mixtures of carbon monoxide and hydrogen are used a marked change in reaction mechanism occurs, and the characteristic production of carbon dioxide is replaced by a production of water. It must be emphasized that this is true only in the case of cobalt and nickel catalysts. When iron catalysts are used, carbon dioxide is the characteristic product, whether pure carbon monoxide or a carbon monoxide-hydrogen mixture is used. Thus, in the case of nickel or cobalt catalysts:

$$CO + 2H_2 = (CH_2) + H_2O \qquad (1)$$

and in the case of iron catalysts:

$$2CO + H_2 = (CH_2) + CO_2. \qquad (2)$$

In order that both reactions (1) and (2) may proceed from left to right, the bonds in the carbon monoxide molecule and the hydrogen molecule must be broken. In addition, the attraction between carbon and hydrogen atoms, between hydrogen and oxygen atoms, and between a molecule of monoxide and an oxygen atom must be greater than the energies of the bonds that are broken. The forces that promote formation of water and those that promote formation of carbon dioxide differ according to the catalyst used. To promote formation of water, a catalyst that activates hydrogen atoms must be chosen; conversely, a catalyst that activates the carbon monoxide molecule must be used if carbon dioxide is to be produced.

87/ Fischer, F., [Collected Papers on the Knowledge of Coal]: Vol. VIII, G. Borntraeger, Berlin, 1927, p. 255.

88/ Tutiya, H., [Catalytic Decomposition of Carbon Monoxide III. Behaviour of Iron Carbides]: Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 556-562; abstracts (in English) published in Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, Nos. 306-309, 1931.

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Antheaume[89] stated that because iron catalysts are used successfully in the form of Fe_3O_4, whereas nickel and cobalt catalysts must first be reduced at 350° C. to 450° C., the difference in the nature of reactions (1) and (2) lies in the presence or absence of reduced metals in the catalysts.

Formation of Free Radicals

When nickel, cobalt, or iron catalysts are carbided with carbon monoxide, and when hydrogen is passed over these carbides, gaseous hydrocarbons, the main constituent of which is methane, are formed, with the complete exclusion of liquid hydrocarbons. The composition of these products, consisting of straight-chain paraffin or olefin hydrocarbons almost entirely, suggests that their formation proceeds via such free radicals as $\dot{C}H$-, $\dot{C}H_2$, and $\dot{C}H_3$, and that these building units are produced by some reaction between carbon monoxide and hydrogen.

As the hydrogenation of carbide produces methane, it is not difficult to conjecture that, while hydrogen is being added to form methane, the steps, $C \longrightarrow \dot{C}H_2 \longrightarrow \dot{C}H_3 \longrightarrow CH_4$ exist. The amount of these free radicals formed depends to a great extent on the reaction temperature and the composition of the catalyst. To form high-molecular-weight liquid hydrocarbons by such a process, much polymerization must occur before hydrogen is added to stop the reaction. The addition of hydrogen to a particle of only a few building units ($\dot{C}H_2$) effectively stops the polymerizing action on that particle, and, if this is a general case, only gaseous hydrocarbons are produced. In other words, a catalyst for the synthesis of gasoline and long-chain hydrocarbons must be more active as a polymerization catalyst than as a hydrogenation catalyst.

Because nickel and cobalt catalysts have high hydrogenating capacities, the formation of gaseous hydrocarbons is always great at the beginning of the synthesis; the production of liquid hydrocarbons is small and becomes significant only after 2 or 3 hours. The author infers that this loss of hydrogenating capacity is accompanied by an increase in polymerizing capacity of nickel or cobalt catalysts, and that it occurs as nickel carbide or cobalt carbide is formed at the active centers of the catalyst. (That is, in the boundary surface between the carbide and the reduced metal, carbide is considered as some sort of polymerization accelerant.) On this basis, a simple explanation may be advanced for the large production of gaseous hydrocarbons that occur during the first stages of synthesis and for the increased production of gaseous hydrocarbons with increase in temperature. For example, if nickel or cobalt catalysts, which have never been processed in reactions, are treated with carbon monoxide-hydrogen mixtures at about 200° C., most of the carbides produced in these catalysts by reaction with carbon monoxide are decomposed largely into methane and metallic nickel or cobalt by reaction with hydrogen; those carbides that are relatively difficult to react with hydrogen at about 200° C. remain. The amount of residual carbides of this type increases with reaction time until, after a given time, the quantity of carbide decomposed by hydrogen equals the quantity of carbide regenerated by the carbon monoxide. The reaction has then attained a constant state, and definite amounts of carbide and reduced nickel or cobalt exist in the catalyst at all times. Because of the inhibiting effect of the carbides on the hydrogenating ability of these metals, a large production of liquid hydrocarbons is obtained.

89/ Work cited in footnote 81.

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The carbide:reduced-metal ratio finally achieved is dependent upon the $CO:H_2$ ratio in the synthesis gas and the reaction temperature. A surplus of hydrogen reduces the quantity of residual carbide and accelerates the formation of gaseous hydrocarbons; a similar effect is achieved with increase in reaction temperature, which increases the reactivity of hydrogen and carbide.

From these observations, it would be concluded that the greater the surplus of carbon monoxide and the lower the reaction temperature, the more the synthesis of liquid hydrocarbons would be favored. Actually, however, exceeding a certain residual-carbide:reduced-metal ratio decreases the regeneration of carbides on the reduced metal, and, hence, a maximum in the production of liquid hydrocarbons cannot be avoided.

As carbides of this type are easily decomposed by hydrogen, the hydrogenation capacity can be increased by increasing the reaction temperature to a suitable degree. However, although the formation of carbides is decreased, because such reactions as $Ni_3C \xrightarrow{CO} Ni_xC \rightarrow XNi + C$ occur at elevated temperatures, free carbon, which is relatively difficult to react with hydrogen, is generated and deposited on the active surface of the catalyst. Thus, the hydrogenation reaction, the rate of which is great in the early stages of synthesis, loses its activity rapidly.

The temperature at which free carbon is produced depends, of course, on the type of catalyst employed and on the composition of the synthesis gas. The quantity of free carbon deposited in the catalyst increases with time and plays an important role in the deterioration of catalyst activity.

Production of Liquid Hydrocarbons from Carbon Dioxide and Hydrogen

The synthesis of liquid hydrocarbons by the catalytic reduction of carbon dioxide was studied by Fischer and Pichler[90] and Koch and Küster[91] and many others, but in all cases methane was produced instead of gasoline. According to Fischer,[92] when nickel-alumina catalyst is used in the methane synthesis, the reduction of carbon dioxide begins at 200° C. whereas the reduction of carbon monoxide does not occur until about 250° C. is reached. However, in the synthesis of liquid hydrocarbons, the carbon dioxide in synthesis gas mixtures of carbon monoxide, hydrogen, and carbon dioxide has no effect whatever on the yield and, without further addition of hydrogen, appears as such in the product gas; the hydrogenation of carbon dioxide is initiated only after any carbon monoxide is totally consumed.

The author has inferred that liquid hydrocarbons are formed under conditions where the hydrogenation capacity of a catalyst is somewhat restricted by carbides produced in the catalyst by reaction with carbon monoxide. Parallel

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90/ Fischer, F., and Pichler, H., [The Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, with Particular Regard to the Synthesis of Hydrocarbons]: Brennstoff Chem., vol. 14, 1933, pp. 306-310.

91/ Koch, H., and Küster, H., [The Catalytic Reduction of Carbon Dioxide with Hydrogen]: Brennstoff Chem., vol. 14, 1933, pp. 245-251.

92/ Work cited in footnote 90.

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reasoning suggests that as carbon dioxide does not enter into any chemical reaction with reduced nickel or cobalt (of course, reduced nickel and cobalt absorb and desorb carbon dioxide at rates which are in equilibrium), no inhibitive effects on its hydrogenation should be considered by virtue of the presence of carbides. Therefore, the carbon dioxide should readily be hydrogenated to methane. However, it has been shown experimentally that at temperatures necessary for appreciable reduction of carbon dioxide all carbon monoxide is quickly consumed by the hydrocarbon synthesis mechanism.

SUMMARY

1. Studies were made of the effects of reaction temperature, gas velocity, and synthesis gas composition on the yield of liquid hydrocarbons, and an optimum reaction temperature and gas velocity were found to exist. A compromise between the most desirable yield of liquid hydrocarbons and the greatest catalyst durability was established at a H_2:CO ratio of 2:1.

2. A ratio of diatomaceous earth to the metals content of the catalyst was found to produce the best results between 1:1 and 3:4; silica gel was also found to be a fair carrier.

3. In the preparation of catalysts, acetates were found to be as good a source material as nitrates.

4. Studies of nickel catalysts showed that by using 100 Ni:20 Mn:8 U_3O_8:4 ThO_2 catalyst, 168.8 ml. of gasoline (C_{5+}) was obtained per cubic meter of synthesis gas.

5. Cobalt-copper catalysts and nickel-cobalt-copper catalysts were investigated. The temperature at which cobalt is reduced does not impair its subsequent catalytic activity in any way. The reduction temperature of cobalt may be lowered from 350° to 200° C. by the addition of more than 5 percent copper; to lower the reduction temperature of nickel from 450° to 250° C., more than 100 percent cobalt and more than 10 percent copper (relative to the nickel) must be added.

6. Studies of catalysts containing silver showed that although silver is inferior to copper as a means of lowering the reduction temperature, it is superior to copper as a promoter.

7. The mechanism of the hydrocarbon synthesis was discussed.

A REVIEW OF INTERNATIONAL RESEARCH ON THE HYDROCARBON SYNTHESIS

Germany

The discovery of the synthesis of hydrocarbons from carbon monoxide and hydrogen is generally credited to Fischer and his associates at Muhlheim, Germany. In 1923, Fischer and Tropsch[93/94] reduced carbon monoxide

93/ Fischer, F., and Tropsch, H., [The Preparation of Synthetic Oil Mixtures (Synthol) from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 4, pp. 276-285.

94/ Fischer, F., and Tropsch, H., [Preparation of Synthetic Oil (Synthol) from Carbon Monoxide and Hydrogen]: Brennstoff Chem., vol. 5, 1924, pp. 201-208, 217-227.

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catalytically at high pressures. Using scrap iron containing alkali, particularly rubidium carbonate, as a catalyst at 400° to 450° C. and 75 to 100 atmospheres' pressure, these workers obtained reaction products containing 10 percent acidic substances, 29 percent of water-soluble alcohols, aldehydes, and ketones, 11 percent of water-soluble oils, and 48 percent of water-insoluble materials. This product they called "synthol." By treatment at 450° C. and high pressures, "synthine," composed chiefly of hydrocarbons, was obtained and proved usable as a substitute for gasoline. Reduction of carbon monoxide was then studied at normal pressures.

Laboratory Research

In 1926, Fischer and Tropsch[95] tested oxides of chromium, zinc, beryllium, rare earth elements, uranium, and magnesium as promoters for iron and cobalt catalysts. They found that the activity was greatest at metal:oxide ratios of 1:1 or 3:1. At about 270° C., 1 cubic meter of water gas (H_2:CO = 1:1) was repeatedly passed over the catalyst to yield approximately 100 gm. of oil (liquid hydrocarbons).[96] Because water gas deactivated the catalyst quite rapidly, coke-oven gas was reacted with steam at high temperatures to give synthesis gas (H_2:CO = 2:1). The most suitable catalyst was found to be 100 Fe:25 Cu:2 K_2CO_3 or 9 Co:1 Cu; 20 to 25 ml. of gasoline (C_{5+}) was obtained with a single pass per cubic meter of synthesis gas. In 1930, Berl and Jüngling[97] studied iron and cobalt catalysts containing copper, zinc oxide, manganese oxide, and potassium carbonate. They found that under their conditions the activity of cobalt catalysts was greater than that of iron catalysts. The same year Fischer[98] found that the presence of alkali was favorable in iron-copper catalysts. By adding a small amount of manganese oxide and alkali to a catalyst of composition Fe:Cu = 4:1, he obtained 40 to 45 ml. of gasoline per cubic meter of $2H_2$:1CO gas; a gasoline yield of 100 ml./m.^{3} was obtained with 9 Co:1 Cu:2 Th catalyst.

It was then discovered that by mixing 2 H_2:1 CO gas and 1 H_2:1 CO gas and using it in the synthesis at a low velocity, a gasoline yield of 50 ml./m.^{3} mixed gas was obtained with iron catalyst and a yield of 130 ml./m.^{3} was obtained with cobalt catalyst. Highly porous substances, such as Stuttgartermasse, were used as carriers for the catalysts in these cases.

In 1931, Fischer and Meyer[99] investigated nickel catalysts and found that thoria and manganese were superior promoters for nickel. Catalysts precipitated from mixed solutions of nitrate salts by sodium bicarbonate or potassium carbonate were most superior, exhibiting an activity comparable to that obtained with catalysts prepared by the calcination of nitrate salts. These investigators advocated using diatomaceous earth as a carrier. In nickel-thoria catalysts, a composition of 100 Ni:18 ThO_2:100 diatomaceous earth, obtained by precipitating from a solution of mixed nitrate salts by potassium carbonate, had the greatest activity, the gasoline (C_{5+}) yield was 120 ml./m.^{3} of synthesis gas. Tests of sodium carbonate, potassium carbonate, ammonium carbonate, caustic potash, and caustic soda showed potassium carbonate to be the best precipitant, with sodium bicarbonate second best;

95/ Work cited in footnote 6.
96/ Work cited in footnote 21.
97/ Work cited in footnote 11.
98/ Work cited in footnote 21.
99/ Work cited in footnote 12.

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caustic potash and caustic soda produced catalysts with almost no activity. Hydrogen reduction was found to be most suitable at 450° C. for 3 hours. Studies of the durability of nickel-thoria catalysts showed that after 5 weeks' use the yield of gasoline was reduced by 12 percent.

In the preparation of nickel-manganese catalysts, potassium carbonate was found to be the best precipitant. A gasoline yield of 120 ml./m.^{3} of synthesis gas was obtained by using a composition of 100 Ni:20 Mn:100 diatomaceous earth; addition of a small quantity of alumina increased this to 130 ml./m.^{3}.

In 1932, Fischer and Koch[1/] studied cobalt catalysts. Corresponding to the results obtained with nickel, thoria and manganese were found to be superior promoters, and, in cobalt-thoria catalysts, potassium carbonate was the best precipitant. A gasoline yield of 153 ml./m.^{3} of synthesis gas was obtained by using a composition of 100 Co:18 ThO_2:150 diatomaceous earth. Hydrogen reduction was found to be most suitable at 350° C. for 4 to 5 hours. In cobalt-manganese catalysts, sodium bicarbonate was found to be superior to potassium carbonate as a precipitant; a gasoline yield of 144.5 ml./m.^{3} of synthesis gas was obtained using a 100 Co:15 Mn:150 diatomaceous earth catalyst.

In 1933, Fischer and Meyer[2/] used 100 Ni:20 Mn:10 Al_2O_3:100 diatomaceous earth catalyst as a standard catalyst in the synthesis of liquid hydrocarbons and clarified the optimum conditions for the precipitation and water wash in the preparation of the catalyst. To a mixed-nitrate solution corresponding to 5 gm. of nickel, potassium carbonate was added, and the resulting precipitate was washed four or five times with 100 ml. of hot water (it was found desirable to leave a minute amount of alkali in the catalyst). Neither graphite (which is considered a good conductor of heat) nor silica gel substances other than diatomaceous earth were found suitable for catalyst carrier purposes. Potassium carbonate was found to be an excellent precipitant. Potato starch was mixed into the catalyst with water, and this material was granulated, placed in the reaction tube, and reduced in hydrogen containing ammonia; a gasoline yield of 140 ml./m.^{3} of synthesis gas was obtained.

Koch and Küster[3/] utilized nickel and cobalt catalysts for the synthesis of gasoline. Attempted reduction of carbon dioxide at various reaction temperatures and gas compositions yielded no liquid hydrocarbons. Fischer and Pichler[4/] observed the effect of carbon dioxide in the synthesis gas; 5 to 10 percent of carbon dioxide was found to have no effect on the yield of liquid hydrocarbons.

In 1934, Fischer and Meyer[5/] made a study of alloy catalysts and found that the catalyst obtained by dissolving out aluminum and silicon by means of caustic soda from alloys consisting of nickel or cobalt (or their mixtures) and aluminum or silicon could be utilized in this reaction. Using 4 gm. of Co-Ni catalyst, 90 ml. of gasoline per cubic meter of synthesis gas was obtained. When this method of preparation was applied to iron catalysts, the

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1/ Work cited in footnote 3.
2/ Work cited in footnote 37.
3/ Work cited in footnote 91.
4/ Work cited in footnote 90.
5/ Fischer, F., and Meyer, K., [Alloy Skeletons as Catalysts for the Synthesis of Hydrocarbons from Carbon Monixde and Hydrogen]: Brennstoff Chem., vol. 15, 1934, p. 107; Ber., vol. 67B, 1934, pp. 253-261.

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results were poor. This type of alloy catalyst has the disadvantage of being less active than precipitated catalysts and of lacking durability; however, it also has the advantage that the activity can be regenerated easily in the event that the catalyst is contaminated with sulfur.

Fischer and Koch[6] and Wiedeking[7] studied the production of lubricating oils from the olefins contained in synthesis gasoline.

Pilot-Plant Work

In 1930, Fischer[8] conducted an experiment on a pilot-plant scale using a synthesis gas obtained by mixing 2 H_2:1 CO gas and 1 H_2:1 CO gas. The gas was purified by removing hydrogen sulfide with iron oxide; organic sulfur compounds were converted into hydrogen sulfide by passage through iron pipes heated to 400° C., and this was scrubbed out in a solution of prussiate salts. The synthesis reaction is violently exothermic, and, as increase in temperature promotes the formation of such gaseous hydrocarbons as methane, ethane, and propane, the heat of reaction had to be dissipated rapidly to prevent the temperature of the catalyst from rising. Fischer paid special attention to this point and tried various reaction chambers.

In 1932, Fischer, Roelen, and Feisst[9] utilizing 100 Ni:20 Mn:10 Al_2O_3:100 diatomaceous earth catalyst and a synthesis gas similar to that just described, conducted an experiment on a pilot-plant scale. A revolving gas-heated reaction tube 155 mm. in diameter and 450 mm. long was used; 890 gm. of catalyst was employed at a reaction temperature of 190° to 200° C., and a gas velocity of 100 liters per hour was used. The results showed a gas contraction of 60 percent and a gasoline (C_{5+}) yield of 80 ml. (65 gm.) per cubic meter of synthesis gas; this value was less than the yield (120 ml./$m.^3$) obtained in the laboratory and was probably due to the highly variable temperature distribution within the reaction tube. Better results were obtained by decreasing the diameter and increasing the length of the reaction tube and by heating it in an electrically heated oil bath instead of with a gas flame. With 70 liters (21.3 kg.) of catalyst at reaction temperatures of 190° to 200° C. and a gas velocity 6.8 $m.^3$/hr., 100 ml. (70 gm.) of gasoline was obtained per cubic meter of synthesis gas, results as good as those obtained in the laboratory (100 ml./$m.^3$) under these conditions. After 1,000 hours' operation, a large amount of solid paraffins collected on the catalyst, necessitating its reactivation by extraction of solid paraffins with gasoline or benzene followed by reduction in hydrogen at 450° C.

6/ Fischer, F., and Koch, H., [The Synthesis of Lubricating Oils from Kogasin. Preliminary Communication]: Brennstoff Chem., vol. 14, 1933, pp. 463-468.

7/ Fischer, F., Koch, H., and Wiedeking, K., [Advances in the Preparation of Lubricating Oils, Starting with Kogasin]: Brennstoff Chem., vol. 15, 1934, pp. 229-233.

8/ Work cited in footnote 21.

9/ Fischer, F., Roelen, O., and Feisst, W., [The Present Technical Position of the Hydrocarbon Synthesis]: Brennstoff Chem., vol. 13, 1932, pp. 461-468.

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Japan

The extensive nature of the studies conducted in Japan on the hydrocarbon synthesis is second only to those made in Germany. The work had its start with Kodama's[10] study at the Kita Laboratory of Kyoto Imperial University. In 1929, the catalytic characteristics of iron, copper, cobalt, and nickel were determined with regard to mixtures of equal volumes of carbon monoxide and hydrogen. These results demonstrated that copper had no catalytic activity, that addition of alumina and manganese oxide to cobalt was deleterious to its activity, that the addition of thoria and copper retarded the decomposition of carbon monoxide ($2CO = C + CO_2$), and that the addition of potassium carbonate accelerated the decomposition of carbon monoxide. The same year, Kobayashi and Yamamoto[11] utilized 100 Co_2O_3:50 CuO:75 MnO catalyst and Kodama[12] utilized 3 Co:1 Cu:0.45 ThO_2 catalyst and obtained, respectively, gasoline yields of 4.9 ml. and 10.2 ml. per cubic meter of 1 H_2:1 CO gas. In 1930, Kodama,[13][14] using cobalt and copper catalysts containing BeO, MgO, ZnO, CaO, TiO_2, ZrO_2, and CeO_2, found that MgO was the best promoter and that the addition of alkali carbonates to iron-copper catalysts was beneficial.[15][16] With 3 Co:1 Cu:0.45 Mn and 100 Fe:10 Cu:2 Na_2CO_3 catalysts, gasoline yields of 44.8 ml. and 21.2 ml., respectively, were obtained per cubic meter of 1 H_2:1 CO gas.

In 1931, Kodama and Fujimura[17] settled on an iron-copper catalyst of composition 100 Fe:100 Cu:0.5 Na_2CO_3 as the best. The same year Fujimura[18] found that variation of the iron:copper ratio from 5:1 to 2:1 produced almost no change in the yield of gasoline. A cobalt-copper-magnesia catalyst of composition Co:Cu:MgO = 4:1:1 was determined as the most suitable of this type, yielding 46.6 ml. of gasoline per cubic meter of 1 H_2:1 CO gas.[19]

10/ Work cited in footnote 70.

11/ Kobayashi, K., and Yamamoto, K., [Synthesis of Petroleum Hydrocarbons from Hydrogen and Carbon Monoxide at Ordinary Pressure]: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 54.

12/ Work cited in footnote 9.

13/ Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure IV. Influence of Beryllium Oxide, Magnesium Oxide, Zinc Oxide, and Cadmium on Cobalt-Copper Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 161; supplemental binding p. 60.

14/ Work cited in footnote 51.

15/ Work cited in footnote 13.

16/ Kodama, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VI. The Formation of Hydrocarbons by Iron Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 33, 1930, p. 1150; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, No. 269, 1930, pp. 169-183 (in German).

17/ Kodama, S., and Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VII. Effect of Alkalies on Iron-Copper Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 32; supplemental binding pp. 14-16 (in German).

18/ Fujimura, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure VIII. The Iron-Copper Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 34, 1931, p. 366; supplemental binding pp. 136-138.

19/ Work cited in footnote 33.

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In 1932, Fujimura,[20] investigating the effect of thorium, uranium, molybdenum, tungsten, chromium, and cerium on cobalt-copper-magnesium catalysts, found thorium and uranium to be the best promoters and obtained a gasoline yield of 81.5 ml. per cubic meter of 2 H_2:1 CO gas in the presence of 8 Co:1 Cu:2 Mg:9.4 U catalyst. In the preparation of Co-Cu-Th and Co-Cu-U catalysts, addition of starch to mixed nitrate salts, followed by evaporating, drying, and calcining, yielded a catalyst of large bulk volume. The largest gasoline yield was obtained with 8 Co:1 Cu:0.5 Th:0.15 U catalyst, the yield of gasoline in this case being 141.0 ml. per cubic meter of synthesis gas; by varying the proportions of thorium and uranium, this value was increased to 145 ml./$m.^3$. In 1933, Fujimura and Tsuneoka[21] observed that the addition of a minute amount of potassium carbonate (about 0.05 percent) to the nickel in nickel-thoria catalysts promoted their activities; conversely, potassium carbonate was found to be harmful to the activities of nickel-manganese catalysts. Rubidium carbonate was found beneficial in both types of catalysts; thus 100 Ni:18 Mn and 100 Ni:18 ThO_2 catalysts to which rubidium carbonate had been added produced a gasoline yield of 108 ml./$m.^3$ of synthesis gas. Addition of chromium, molybdenum, uranium, and thorium to nickel-manganese catalysts[22] demonstrated that, with increase in the atomic weight of the added metal, an increase occurred in promoting action; thorium was determined as the best promoter. Catalysts having the compositions 100 Ni:15 Mn:3 ThO_2 and 100 Ni:50 Mn:3 Al_2O_3 produced gasoline yields of 137 ml. and 130 ml., respectively, per cubic meter of synthesis gas. When 0.5 percent of copper (relative to nickel) was added, virtually no change was produced in the yield of gasoline; as this was increased to 1 percent, the gasoline yield gradually decreased. An optimum copper content of 0.5 percent was thus established.

In 1934, Fujimura and Tsuneoka[23] discussed the composition of the products of the synthesis. They found small quantities of acids, alcohols, aldehydes, and ketones in the water formed in the reaction. These investigators also studied the effects of sulfur compounds on nickel catalysts[24] and found that whereas a small amount of hydrogen sulfide or carbon disulfide stimulated the catalytic activity of Ni-Mn-Al_2O_3 catalysts and increased the yield of gasoline, these materials were quite harmful to Ni-Mn-ThO_2 catalysts. Studies of the effects of synthesis gas composition[25] indicated that 2 H_2:1 CO gas was most suitable. Although excess carbon monoxide had no ill effects on the gasoline synthesis, an excess of hydrogen was found to be deleterious, in that such an excess caused a shift in reaction mechanism from the synthesis of

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20/ Work cited in footnote 36.
21/ Work cited in footnote 31.
22/ Work cited in footnote 48.
23/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XVII. The General Properties and Chemical Composition of the Reaction Products]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 115; supplemental binding pp. 49-51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 79-92.
24/ Fujimura, K., Tsuneoka, S., and Kawamichi, K., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XVIII. The Effect of Sulfur Compounds on Nickel Catalysts]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 920; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 93-102.
25/ Work cited in footnote 26, p. 15.

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gasoline to the synthesis of methane. Watanabe, Morikawa, and Igawa[26] of the Central Laboratories of South Manchurian Railway Co., discussed quantitative relationships in the hydrocarbon synthesis. These workers also observed (1) the effects of reaction temperature[27] and found that the production of liquid hydrocarbons and water and the gas contraction are similarly affected; (2) the effects of the reduction temperature on activity, and found that for cobalt-copper catalysts 200° to 250° C. was most suitable for reducing the carbonate salts, and 190° to 200° C. was most suitable for reducing the oxides.

Fujimura and Tsuneoka[28] observed the effects of the presence of nitrogen, methane, and carbon dioxide in the synthesis gas and found that their only effect was that of a diluent.

Tsuneoka[29] studied the relationship between the synthesis gas composition and both the reaction temperature and the degree of product saturation and found that at H_2:CO ratios greater than 2:1, the reaction could be accelerated by increasing the temperature. At H_2:CO ratios less than 2:1, however, the formation of methane could be inhibited by lowering the reaction temperature. The iodine values of the liquid hydrocarbon product indicated that an excess of hydrogen considerably increased the saturation of the product. Tsuneoka also investigated alloy catalysts[30] and obtained a gasoline yield of 108 ml./m.^{3} of synthesis gas by using a catalyst prepared by dissolving out the silicon from a 1 Ni:1 Co:2 Si alloy by means of caustic soda.

Britain

No significant research on the hydrocarbon synthesis has been carried out in Britain.

In 1926-1927, Elvins[31/32], using synthesis gas consisting of 54.6 percent of hydrogen and 44.8 percent of carbon monoxide and employing Co-Cu-Mn

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26/ Watanabe, S., Morikawa, K., and Igawa, S., [Synthesis of Hydrocarbons by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure I. Methods of Synthesis and Analysis]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 317; supplemental binding pp. 142-146.

27/ Work cited in footnote 13, p. 6.

28/ Fujimura, K., and Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XX. Composition of the Initial Gas Mixture]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1543; supplemental binding pp. 704-711; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 127-136.

29/ Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XXI. Relation of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Products]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1548; supplemental binding pp. 711-716; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 137-143.

30/ Tsuneoka, S., [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XXII. Efficiency of a New Alloy Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 1608; supplemental binding pp. 144-151.

31/ Work cited in footnote 22, p. 15.

32/ Elvins, O., and Nash, A., Synthetic Fuel from Carbon Monoxide and Hydrogen: Fuel in Sci. and Practice, vol. 5, 1926, pp. 263-265.

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catalyst (5- to 10-mesh) and at a gas velocity of 6.2 liters per hour with an average reaction temperature of 286° C., obtained from 2.077 cubic meters of synthesis gas, 2.5 gm. of vaselinelike solids, 3.4 gm. of "yellow oil," 1 ml. of water, and 8.15 gm. of insoluble matter. (This corresponds to a yield of 7 gm. of liquid hydrocarbons per cubic meter of synthesis gas.

In 1928, Erdley and Nash,33/ using cobalt and copper catalysts promoted with alumina, zinc oxide, and manganese oxide, found Co-Cu-ZnO to be superior, yielding 7.9 ml. of liquid hydrocarbons per cubic meter of synthesis gas.

The United States

In the United States, as in Britain, no significant research has been carried out on this problem.

In 1928, Smith, Davis, and Reynolds34/35/ investigated copper-containing catalysts. According to their results, Co-Cu-U catalyst was most effective and yielded 0.68 ml. of liquid hydrocarbons from 10.7 liters of 1 H_2:1 CO gas at a temperature of 275° C. A detailed study was made of the properties of the hydrocarbons formed with Co:Cu:Mn catalyst and of the quantity of water gas converted. These investigators found that an excessive temperature was harmful to the catalyst; 18.4 ml. of liquid hydrocarbons was obtained from a liter of water gas by using 2.5 Co_2O_3:0.6 CuO:0.5 MnO catalyst.

France

In 1933, Decarriere and Antheaume36/ investigated iron catalyst in the hydrocarbon synthesis. Using 4 Fe:0.1 Cu catalyst, they obtained liquid hydrocarbon yields of 37 gm./$m.^3$ of synthesis gas when the catalyst did not contain potassium carbonate, and when the catalyst did contain potassium carbonate 22 gm./$m.^3$ were obtained. These results contradict Fischer's, which indicate that alkali carbonates exert a promoting effect upon iron-copper catalysts.

In 1934, Antheaume, Decarriere, and Réant37/ studied iron-copper catalysts by X-ray analysis and found that the catalyst that had the highest activity consisted almost entirely of Fe_3O_4, with an extremely small amount of Fe_2O_3 present; they found no metallic iron in any case.

33/ Work cited in footnote 7, p. 6.
34/ Work cited in footnote 10, p. 6.
35/ Smith, D. F., Hawk, C. O., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas, II: Ind. Eng. Chem., vol. 20, 1928, pp. 1341-1348.
36/ Decarriere and Antheaume, J., [An Iron Catalyst for Hydrogenation of Carbon Monoxide at Ordinary Pressures]: Compt. rend., vol. 196, 1933, pp. 1889-1891.
37/ Work cited in footnote 81.

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